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Evaluation of FGD (Flue Gas Desulfurization) Dry Injection Sorbents and Additives Volume 1. Development of High Reactivity Sorbents

Acurex Corp., Research Triangle Park, NC

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16. ABSTRACT: The report discusses recent work addressing lime enhancement by slurrying with siliceous materials and testing in a laboratory packed-bed reactor, as part of EPA's efforts to develop low cost, retrofit flue gas cleaning technology, including the development of highly reactive sorbents. The solids generated from a furnace limestone injection process were reactivated by slurrying at elevated temperatures. Compared with untreated solids, reactivity toward SO2 was significantly enhanced by hydration. The SO2 capture by solids increased with increasing time and temperature of hydration. The SO2 capture was probably enhanced by the calcium aluminate silicate hydrates formed during the slurrying process. In addition to flyash, silica from alternative sources was reacted with lime. The dry sorbents produced by slurrying several diatomaceous earths, or montmorillonitic clays, with lime were found to be highly reactive with SO2. The most reactive sorbent was generated by slurrying silica/lime at a weight ratio of 1 to 1. The morphology of the developed sorbents was characterized. Several additives were tested to evaluate their potential to promote the lime/silica reaction rate and increase sorbent reactivity. The maximum enhancement effect was obtained by using 4 to 8 mol % additives. The optimum temperature range for pressure hydrating flyash with lime was 110-160°C.

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EVALUATION OF FGD DRY INJECTION SORBENTS AND ADDITIVES

VOLUME 1

DEVELOPMENT OF HIGH REACTIVITY SORBENTS

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ABSTRACT

EPA's efforts to develop low cost, retrofit flue gas cleaning technology include the development of highly reactive sorbents. Recent work addressing lime enhancement by slurrying with siliceous materials and testing in a laboratory packed bed reactor is discussed in this report.

The solids generated from a furnace limestone injection process were reactivated by slurrying at elevated temperatures. Compared with untreated solids, reactivity toward SO_2 was significantly enhanced by hydration. The SO_2 capture by solids increased with increasing time and temperature of hydration. The SO_2 capture was probably enhanced by the calcium aluminate silicate hydrates formed during the slurrying process.

In addition to flyash, silica from alternative sources was reacted with lime. The dry sorbents produced by slurrying several diatomaceous earths, or montmorillonitic clays, with lime were found to be highly reactive with SO_2. The most reactive sorbent was generated by slurrying silica/lime at a weight ratio of 1 to 1. The morphology of the developed sorbents was characterized.

Several additives were tested to evaluate their potential to promote the lime/silica reaction rate and increase sorbent reactivity. Of the four additives tested, NaOH, $Na_2HPO \cdot 7H_2O$, $(NH_4)_2HPO_4$, and H_3PO_4 were found effective in enhancing the flyash/lime reaction. The maximum enhancement effect was obtained by using 4 to 8 mol percent additives.

Pressure hydration of flyash and lime fostered the formation of a reactive sorbent much quicker, and used less flyash, than did atmospheric hydration. The reactivity of the sorbent in the packed bed reactor correlated well with B.E.T. surface area, increasing with increasing surface area. The optimum temperature range for the pressure hydration of flyash with lime was between 110 and 160 °C (230 and 320 °F).

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SECTION 1

EXECUTIVE SUMMARY

1.1 INTRODUCTION

Highly reactive sorbents are needed for the dry sorbent injection flue gas desulfurization (FGD) process. The dry sorbent injection concept is very attractive, especially for retrofitting existing power plants, because of its technical simplicity and low capital cost. However, due to limited space and the high velocity of flue gas, an extremely short gas/solid reaction time is available for SO_2 absorption. As a result, very low utilization (less than 30 percent) was obtained by using a conventional sorbent such as lime. Better sorbent utilization could be achieved when the sodium based sorbents, such as nahcolite and trona, were used. Sodium salts generated from FGD processes possess much higher solubility in water (12.5 g of Na_2SO_3 per 100 g of cold water) than do calcium salts (0.0043 g of $CaSO_3 \cdot 1/2H_2O$ per 100 g of cold water), and therefore may constitute the environmental hazard of leaching salts into ground water if the waste is disposed in landfills.

Calcium silicate hydrates produced by pozzolanic reaction between silica and lime in water at elevated temperatures are very attractive calcium based sorbents for dry injection processes. When prepared in appropriate forms, these hydrates are very reactive with SO_2 and should result in good sorbent utilization. Previous study (Jozewicz and Rochelle, 1985) has shown that reactive calcium silicate hydrates can be produced by slurrying flyash with lime at temperatures below 100 °C (atmospheric hydration), but relatively high flyash/lime ratios (greater than 3) and long reaction times (longer than 8 h) are required. For commercial application this method might not be viable. A high flyash/lime ratio would increase flue gas duct loading and overload the particulate control device. The long reaction time would increase the reactor size and capital cost. One of the objectives of this work was to evaluate potential techniques of reducing the flyash/lime ratio as well as the reaction time.

Another objective was to apply the concept of using silica/lime sorbent to reactivate solids from furnace limestone injection processes to enhance the overall SO_2 removal and promote waste utilization.

The major experimental apparatus used was a laboratory-scale packed bed reactor. The glass reactor (45 mm in diameter, 150 mm in length) was packed with powdered sorbent mixed with 70-mesh sand to prevent channeling. The reactivity of various sorbents was measured by the quantity of SO_2 absorbed under typical dry injection flue gas conditions. Reagent grade $Ca(OH)_2$ was used as the baseline sorbent. Calcium silicate hydrates were prepared by pressure hydration or by slurrying siliceous materials with lime in a stirred beaker immersed in a thermostated water bath. After mixing, the samples were vacuum filtered and dried before testing in the reactor. A stainless steel high pressure 300 mL vessel was used to prepare the calcium silicate hydrates at temperatures above 100 °C (212 °F) (pressure hydration). The high pressure vessel was heated electrically and its temperature controlled by a thermocouple. Sorbent reactivity was calculated in terms of SO_2 capture and lime conversion. The SO_2 capture was defined as the amount of SO_2 absorbed per unit weight of sorbent (mmol SO_2/g). Lime conversion was the percent of lime in the sorbent which reacted with the absorbed SO_2, assuming $CaSO_3$ was the product.

1.2 REACTIVATION OF BOILER LIMESTONE INJECTION SOLIDS

The objective of this segment of work was to apply the pozzolanic reaction concept to Boiler Limestone Injection Solids (BLIS). Their potential for producing reactive sorbent to increase overall SO_2 capture and sorbent utilization was evaluated.

Due to the low sorbent utilization of boiler limestone injection processes, BLIS usually contains significant amounts of unreacted lime. Other ingredients include calcium sulfate, limestone, and flyash. Six samples of BLIS, produced in 1981 by boiler limestone injection experiments, were tested. The untreated BLIS showed virtually no SO_2 removal capability in the packed bed reactor. Hydrating the BLIS at elevated temperatures for a prolonged period of time was tested as a means of reactivating these solids.

For the BLIS samples hydrated at 65 and 90 °C (149 and 194 °F) over 1 to 8 h intervals, the SO_2 capture increased with increased time of hydration, but leveled off at about 1.8 mmol SO_2/g. X-ray

elemental analysis of hydrated samples showed Al, S, and Ca peaks, suggesting that ettringite or other synthetic calcium aluminate sulfate crystals were formed during hydration. X-ray powder diffraction analyses confirmed the existence of those crystals and further suggested that they were hydrated crystals with a high water content. A significant increase of solid surface area by hydration was measured by B.E.T. analyses. The initial value for untreated BLIS was 2.67 m^2/g. The surface area of hydrated BLIS reached as high as 50.86 m^2/g. The surface area increased with both hydration time temperature. A good correlation was obtained between the developed surface area and the reactivity of the hydrated BLIS.

1.3 SCREENING OF ALTERNATIVE SOURCES OF SILICA

The objective of screening alternative silica sources was to evaluate the reactivity of various siliceous materials with lime. The siliceous materials evaluated included cryptocrystalline forms of silica such as diatomaceous earths, tripolis, and pumices. Several grades of naturally occurring bentonitic clays and kaolins were also tested. Each sample of the siliceous materials tested was hydrated with lime at 90 °C (194 °F). The reactivity of the hydration product was evaluated in the bench-scale packed bed reactor.

The hydrates produced from the natural grade diatomaceous earths were more reactive than those from calcined earths. The calcination of diatomaceous earths used in commercial products, especially when sodium salts were used as an additive, caused an 80 percent decrease of B.E.T. surface area. Sodium based additives used during calcination probably caused sintering at the high temperatures [above 900 °C (1,652 °F)] in the kiln, producing siliceous slag on the surface of diatomaceous earth similar to the glassy layer on the surface of flyash particles.

The hydrates produced from naturally occurring bentonitic clays were also found to be more reactive than those from treated or "activated" clays. Hydrates from kaolins generally performed more poorly than bentonitic clays.

Parametric tests were conducted with the two most promising alternative siliceous materials—MN-53 (a diatomaceous earth) and Bentonite 149 (a bentonitic clay). The most reactive hydrates were

produced by reacting siliceous materials with lime at a silica/CaO ratio of about 1. Most likely, the calcium silicate was formed during the hydration process according to the following hypothetical reaction:

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 \cdot H_2O$$

Assuming the relative reactivity toward SO_2 being in the order: $CaSiO \cdot H_2O > Ca(OH)_2 > SiO_2$, only at equimolar condition can the greatest amount of the most reactive hydrates be produced. X-ray powder diffraction analysis confirmed that $Ca(OH)_2$ and SiO_2 disappeared after hydration. The less unreacted the $Ca(OH)_2$ was, the more reactive were the hydrates.

1.4 EFFECTS OF ADDITIVES ON SORBENT REACTIVITY

The objectives of this segment were to evaluate the effectiveness of additives in enhancing reactivity of hydrates produced by flyash/lime slurrying. The additives tested included sodium hydroxide, sodium phosphate, ammonium phosphate, and phosphoric acid. Sodium hydroxide has the potential of enhancing the reaction rate between flyash and lime by increasing the solubility of silica. Phosphates could promote the flyash/lime reaction by increasing the flyash dissolution rate resulting from their ability to attack the glassy layer on flyash particle surfaces.

Sodium hydroxide tests were performed at a flyash/$Ca(OH)_2$ ratio of 2.3 to 1. The enhancement effect was reflected by an increase of lime conversion from 35 to 50 percent when comparing the reactivity of hydrates prepared with and without sodium hydroxide addition. The maximum enhancement effect was obtained with a dose of 4 mol percent of NaOH additive (based on Na/Ca ratios). The higher the sodium hydroxide concentration in the flyash/lime slurry, the more pronounced the enhancement effect.

Three phosphates, $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and H_3PO_4 were tested. All data showed that the maximum enhancement occurred when a dose of 4 to 8 mol percent phosphate (based on PO_4/Ca ratios) was used to slurry the flyash with lime. When CaO instead of $Ca(OH)_2$ was slurried with flyash, the amount of phosphate needed to reach the same degree of reactivity was 50 percent and 70 percent, respectively, when $(NH_4)_2HPO_4$ and $Na_2HPO_4 \cdot 7H_2O$ were used. For example, a maximum lime conversion of 50 percent was reached when 4 and 8 mol percent of $(NH_4)_2HPO_4$ were

respectively added during the slurrying of flyash with CaO and $Ca(OH)_2$. The result may stem from the dispersing properties of phosphates, present during the hydration of CaO, which create finer particles in the product compared to those obtained using $Ca(OH)_2$.

1.5 PRESSURE HYDRATION EVALUATION

Pressure hydration was evaluated as a means to produce calcium silicate hydrates for dry SO_2 control. The focus was on the pressure hydration of flyash or diatomaceous earth with $Ca(OH)_2$, aimed at reducing the time of hydration and the weight ratio of siliceous materials to lime.

Pressure hydration is used commercially to hydrate dolomitic lime (CaO + MgO), as MgO usually is difficult to hydrate completely within a reasonable period of time under atmospheric conditions. Pressure hydration allows the use of high temperatures (above 100 °C) and high pressure (above 1 atm) to accelerate the reaction rate. For the silica/lime reaction, the high temperature of pressure hydration increases the silica solubility and enhances the pozzolanic reaction rate.

Comparing atmospheric hydrates with pressure hydrates, the data clearly showed that a significant decrease of time of hydration is possible when the hydration temperature is increased. For example, atmospheric hydration at 90 °C (194 °F) for 8 h was required to enhance the conversion of $Ca(OH)_2$ up to 35 percent, when the weight ratio of flyash to $Ca(OH)_2$ was 2.3 to 1. The same conversion was achieved for the same reactants and weight ratio after they had been pressure hydrated at 150 °C (302 °F) for 1 h. Pressure hydration could also reduce the flyash/lime weight ratio requirement. At a flyash/lime ratio of 1, the product of pressure hydration at 120 °C (248 °F) for 2 h showed 45 percent lime conversion. The atmospherically hydrated product at the same flyash/lime ratio never achieved the 45 percent lime conversion.

The present work also included pressure hydration of diatomaceous earth/CaO slurry at 150 and 230 °C (302 and 446 °F) for about 1 h. No significant increase in reactivity (lime conversion) was achieved by pressure hydration of diatomaceous earth with lime.

Parametric tests were conducted to pressure hydrate the lime with flyash. There is an optimum hydration time for each hydration temperature. At 230 °C (446 °F), the maximum reactivity (lime conversion) was obtained with about 1 h hydration of flyash/lime at a ratio of 2.3. The optimum hydration

time became 4 h at 180 °C (356 °F), and 5 h for 150 °C (302 °F). When the flyash/lime ratio decreased from 2.3 to 1, the optimum hydration time shifted from 5 h to 1 h at 150 °C (302 °F).

The reactivity of pressure hydrated flyash/lime correlated quite well with B.E.T. surface area. Higher surface area hydrates, generally produced at medium temperatures [150~180 °C (302~356 °F)], optimum hydration time, and relatively high flyash/lime ratio (e.g., 2.3), usually possess greater reactivity toward SO_2.

The crystal morphology of the pressure hydrated flyash/lime mixtures was examined by scanning electron microscope (SEM) and x-ray diffraction. Compared with B.E.T. surface area and reactivity data, two factors were found necessary for the hydrates to readily react with SO_2 under conditions encountered in a dry injection FGD process: large sorbent surface area and amorphous surface structure. Usually, highly reactive hydrates have a large surface area and a gel-like amorphous crystal surface. There was one hydrate sample prepared at 230 °C (446 °F), even though the measured B.E.T. surface area was high (17 m^2/g), the reactivity was poor (16 percent lime conversion). SEM pictures showed that instead of gel-like amorphous materials, a framework of distinct needle-shaped crystals was found. This finding seemed to indicate that the reactivity of hydrates was a function of crystal structure, which could be affected by hydration temperature.

1.6 CONCLUSIONS

Experimental results from the current study have indicated that the waste solids from a boiler limestone injection process can be reactivated by atmospherically hydrating them under conditions which permit the reaction of calcium with silica to form large surface area hydrates. New crystals (calcium/aluminate/silicate/sulfate hydrates) were found in the reactivated BLIS samples. The reactivity of these hydrated BLIS samples increases with the time and temperature used for hydration, and correlates well with surface area, i.e., increases with increasing surface area. The reactivity of these hydrated BLIS samples is sensitive to the relative humidity of flue gas, with the SO_2 reactivity increasing relative humidity.

Siliceous materials from sources other than flyash were found effective in enhancing the reactivity of the sorbents produced by slurrying with lime at elevated temperatures. Among the siliceous materials

tested, natural grade diatomaceous earth and bentonitic clay were found to be the most effective in producing reactive hydrates with lime. The most reactive hydrates were produced by slurrying siliceous materials with lime at a silica/CaO ratio of about 1. It is postulated that calcium silicate hydrates were formed during the slurrying process. The high reactivity of the slurrying product can be partially attributed to the large surface area of calcium silicate hydrate and its high water retaining capability.

Additives such as sodium hydroxide, sodium phosphate, ammonium phosphate, and phosphoric acid can be added to the flyash/lime slurry to enhance the reactivity of the produced hydrates. The maximum reactivity enhancement effect was obtained by using 4 to 8 mol percent (versus Ca) additives.

Very reactive sorbents for dry injection SO_2 removal from flue gas can be produced by pressure hydration of flyash with lime. Pressure hydration fosters the formation of hydrates from flyash/lime slurry in much less time than does atmospheric hydration. Hydration time, temperature, and flyash/lime ratio are the three major parameters which affect the reactivity of the hydrates. Matrices of optimum pressure, hydration time, temperature, and flyash/lime ratio for dry injection SO_2 removal purpose are needed for commercial application. SEM and x-ray diffraction studies demonstrated the formation of hydrates of different morphologies by using different flyash/lime ratios and changing the conditions of pressure hydration. Both high B.E.T. surface area and amorphous surface structure are necessary characteristics for the hydrates to be reactive with SO_2. Although hydrates with well-defined, needle-shaped crystals have a large surface area, they are not reactive with SO_2.

SECTION 2

INTRODUCTION

Dry sorbent injection into flue gas ductwork is an attractive retrofit option for controlling SO_2 emissions from coal-fired boilers and abating potential acid rain precursors. In the process, sorbent particles are introduced in humidified and/or temperature-controlled flue gas in ducting between the air preheater and the particulate control device. Total removal of SO_2 during this process is the sum of the removal in the duct and in the particulate collector [either a fabric filter (FF) or electrostatic precipitator (ESP)].

A number of proof-of-concept demonstration tests have been sponsored by the Department of Energy (DOE), the Environmental Protection Agency (EPA), and the Electric Power Research Institute (EPRI) (Muzio and Offen, 1987). Preliminary results indicated that the sorbent utilization of the dry injection process was usually less than 30 percent. The reasons for the relatively low sorbent utilization include an extremely short (less than 2 s) duct residence time, less than ideal mixing, and the relatively slow gas/solid reaction rate. The sorbent utilization was usually lower when an ESP rather than a FF was used as the particulate collection device. The SO_2 removal in the ESP is limited to a low level by the bulk gas phase SO_2 mass transfer to the layer of sorbent on the collection plate (Yoon et al, 1985a). However, at existing power plants, which may need to be retrofitted for SO_2 control, ESP's are encountered more frequently than FF's. One obvious way of overcoming the lower SO_2 capture of ESP's is to develop a new generation of sorbents which offer greater reactivity towards SO_2. As a result, a significant portion of the overall system removal of SO_2 would take place in the duct, achieving better sorbent utilization.

2.1 ENHANCEMENT OF LIME BY SILICA

A previous study (Jozewicz and Rochelle, 1986) has shown that the reactivity of lime toward SO_2 can be enhanced by mixing lime with materials containing silica in water at elevated

temperatures for a minimum of 8 h. The most obvious and abundant source of silica in power plants is flyash. The reaction of flyash (or other siliceous material) with lime in the presence of water is called the pozzolanic reaction. Calcium aluminum silicate hydrates are the most likely products of this reaction. The nature of calcium silicate hydrate and calcium aluminate hydrate formation, as well as that of calcium aluminum silicate hydrate in the CaO-SiO_2-Al_2O_3-H_2O systems, is very complicated. It is usually impossible to assign a simple chemical formula to it (Taylor, 1950). At temperatures from about 20 to 100 °C (about 68 to 212 °F), two main calcium silicates are formed—calcium silicate hydrate and dicalcium silicate hydrate. Their ratio and extent of formation depend on the ratio of calcium-to-silica in the slurry, as well as on the concentration of CaO in solution (Steinour, 1947). In the early stage of formation, calcium silicate hydrates produced from CaO and amorphous silica are fibrous gels, and their surface area is in the range of 100 to 300 m^2/g (Kantro et al, 1961). Reaction of flyash and $Ca(OH)_2$ yielded products with surface areas up to 140 m^2/g, depending on the length of reaction time and the flyash/$Ca(OH)_2$ ratio (Tognon and Ursella, 1981).

The detailed reaction mechanisms between SO_2 and the flyash/lime derived sorbents are still under investigation. The large surface area calcium silicate hydrates are essential to high reactivity by providing a large gas/solid contact area and, possibly, local high moisture content. During this segment of research, the principles of silica/lime enhancement were applied to the reactivation of solids from furnace injection of limestone for SO_2 control.

The direct injection of calcium compounds into coal-fired furnaces/boilers for controlling SO_2 emissions has been of environmental interest for some time because of its relatively low capital cost. Recent studies discuss the potential of this control technology (Martin and Abbott, 1985) and also report on efforts to understand the mechanism of SO_2 capture in the furnace (Borgwardt et al, 1985 and Thompson, 1985). If proven economically attractive for meeting mandated SO_2 control levels, direct injection of limestone into the furnace could become the predominant means of reducing the emissions of SO_2 from the combustion of coal. However, a too low sorbent utilization would make the benefits of low capital and operating costs for SO_2 capture less attractive. For example, during tests at Du Pont's Martinsville, VA, plant, the limestone utilization (percentage of sorbent that actually reacts with SO_2 to

form sulfite/sulfate products) was 18 to 20 percent, with 50 percent SO_2 removal at stoichiometric ratios of 2.75 to 2.5 (Fink et al, 1985). A higher sorbent utilization leading to lower stoichiometry and more effective SO_2 removal seems necessary to make this control technology competitive with commercial flue gas desulfurization systems.

The highest apparent limestone utilization achieved during the 1981 tests at Hoot Lake Station in North Dakota (operated by Otter Tail Power Company) was 15 percent, at a ratio of calcium in the limestone to the sulfur in the lignite (stoichiometry) of 2, with SO_2 removal of 27 to 29 percent at average flue gas SO_2 concentration of 640 to 700 ppm (Blythe, 1982). Utilization was described as the ratio of moles of sulfur captured to the moles of calcium injected into the boiler. These results differed greatly from the test goal of at least 50 percent SO_2 removal at a stoichiometry of 2. To satisfy this goal, additional removal of SO_2 would be needed between the boiler and the stack, with the most apparent locations for additional SO_2 removal being in the duct from the boiler to the particulate control device and in the device itself.

While in the boiler/furnace, the injected solids will react with other materials to form gaseous and solid products. These reactions may activate certain compounds that combine with SO_2. For example, the thermal environment in the boiler/furnace leads to some calcination of limestone, and the resulting lime may react with SO_2. The flyash formed during combustion may contain alkaline material, depending on the type of coal fired, which can also capture SO_2 in the boiler/furnace. The foregoing reactions will unlikely go to completion because of reagent blinding or other inhibiting effects. Consequently, potential sorbents may be made available from inactivated materials (products) leaving the boiler/furnace. These products contain unreacted limestone, lime formed by calcination in the boiler, sulfated sorbent, and flyash. If these products, which under normal conditions are considered to be wastes, can be reactivated to absorb SO_2 during its residence time in the duct and particulate control device, the resulting sorbent would improve the SO_2 capture of the overall boiler limestone injection process. Increased sorbent utilization, through reactivation of these products and their use in a dry sorbent injection process, would beneficially use large quantities of normally wasted material.

During this work, six sample products from a previous furnace limestone injection test were reactivated according to the silica/lime enhancement principles. The results are reported in Section 4.

2.2 ALTERNATIVE SOURCES OF SILICA

In addition to flyash, there are a number of other siliceous materials which have the potential of being alternative sources of silica for pozzolanic reaction with lime. Cryptocrystalline forms of silica and aluminosiliceous clays were considered as primary alternative sources of silica. Cryptocrystalline forms of silica include diatomaceous earth, tripoli, and pumice. Diatomaceous earth (diatomite, kieselguhr) is a sedimentary rock composed of siliceous shells from a flowerless plant of the class Bacillarieae. Initially, silica in diatomaceous earth was amorphous, but many of the known deposits are millions of years old so that the silica may be present as cryptocrystalline quartz. The particles are very fine and have a large surface area (Neu and Alciatore, 1978). The silica content may be as high as 94 percent, but it depends on the purity of the batch (Hull et al, 1958). Another interesting property of diatomaceous earth is that it can retain up to 2 to 3 times its own weight of water. There are two main types of commercially available diatomaceous earth: natural and calcined. Calcined material is heat treated at about 900 °C (1,652 °F), sometimes with the addition of anticaking agents such as sodium compounds.

Tripoli and pumice, which are other forms of microcrystalline silica, are of volcanic origin (Meisinger, 1983). Their properties should be similar to the large surface area amorphous silica mined at Pozzuoli, Italy during the Roman Empire. Even today, Italian pozzolanas are mined and widely used as a concrete admixture superior to flyash in their ability to combine with free lime (Costa and Massazza, 1983).

Clay is a very abundant material in the earth's crust. It is fine grained and composed of a group of crystalline minerals known as the clay minerals. These minerals are hydrous silicates, and some contain iron, alkalies, and alkaline earths (Ampian, 1983). The U.S. Bureau of Mines classifies clays into six groups: kaolin, ball clay, fire clay, bentonite, fuller's earth, common clay, and shale. Of these, kaolin and bentonite may be of interest in FGD. Ball clay and fire clay are mainly kaolinite (kaolinite is a kaolin mineral, others are, for example, dickite, halloysite, or serpentinite). Fuller's earth contains distinct

needle-shaped attapulgite, and therefore it may possess environmentally unacceptable asbestos-like properties.

Kaolinite consists of distinct layers of silica and alumina, and may be formed by the weathering of potassium and sodium feldspars. Its general chemical formula is $Al_2(OH)_4Si_2O_5$. However, kaolinite may have Mg and/or Fe intrusions. Conventionally, it is used as a raw ceramic material, as well as a filler in the paint, paper, and rubber industries (Bentalspacher and Van der Marel, 1968).

Bentonite is a rock composed largely of montmorillonite from the montmorin group of minerals. Montmorillonite consists of successive layers, each formed by one Al-sheet enclosed between two Si-sheets (Grim, 1953). When treated with H_2O, montmorillonite will swell because of its large surface area (400 to 800 m^2/g), the large amount of exchangeable cations (Na^+, Ca^{++}), and the poor ordering of several layers. The general formula of montmorillonite is $(Al, Mg, Na, Fe)_2 (OH)_2 Si_4O_{10} \cdot H_2O$ (where n, the number of molecules, varies depending on the clay's environment conditions). Sometimes clays are activated with acids which solubilize structural cations and result in the opening of the clay structure and increased surface area. It has been shown that a reaction of $Ca(OH)_2$ with clays at room temperature and at 39 °C (102 °F) gives tetracalcium aluminate hydrates and silicates, among other products (Van Aardt and Visser, 1977).

Another possible silica source of natural origin may be bauxite, meant here as any sediment rich in alumina. Of special interest would be early geological forms of bauxite—terra rosa (about 40 percent SiO_2 and about 30 percent Al_2O_3) and terra fusca (about 45 percent SiO_2 and about 25 percent Al_2O_3) (Valenton, 1972).

Deposits of natural clays are abundant, and in 1983 almost 41 Mt were sold in the U.S. (Ampian, 1983). Out of this number, 3 Mt were bentonite and 7 Mt were kaolin. Deposits of common clay and shale are widespread all over the country. However, kaolins predominate in the East (Georgia, South Carolina) while bentonites are more common in the West (California, Wyoming). Some are also found in Texas, Nevada, and Mississippi.

Aside from flyashes, silica fume could be an artificial source of silica. It offers the advantage of extremely fine particles (90 percent below 0.7 μm) (Aitcin, et al, 1983).

The alternate sources of silica selected for testing in this work include cryptocrystalline forms of silica and aluminosiliceous clays. The results are presented in Section 5.

2.3 ADDITIVES

When flyash and lime were slurried, a high flyash/lime ratio (greater than 3) is required to produce reactive sorbents. The high flyash/lime ratio is caused by the low dissolution rate of siliceous materials in flyash. One possible way to obtain reactive flyash/lime sorbent, while keeping the weight ratio low, would be to use additives to increase the dissolution rate of flyash. The flyash dissolution rate is limited by at least two factors: the extremely low solubility of silica and the relatively inert glassy layer on the surface of flyash particles (Sersale, 1980). Sodium hydroxide can be used as an additive to raise the slurry pH to increase the silica solubility. Previous research (Van Lier et al, 1960 and Alexander et al, 1953) indicated that the measured solubility of finely ground quartz particles in water was 0.9×10^{-3} mol SiO_2/kg water at 90 °C (194 °F). In 0.1 N NaOH solution, the solubility increased to 6.7×10^{-3} mol SiO_2/kg water. Another potential additive is phosphates. Phosphates were reported to facilitate the breaking and dissolution of the glassy layer of flyash, increasing its pozzolanic activity and the overall amount of silicate produced (Bergeseon et al, 1984 and Santoro et al, 1986). The results of the current additive tests are discussed in Section 6 of this report.

2.4 PRESSURE HYDRATION

Pressure hydration was evaluated during this work as a means to decrease the weight ratio of siliceous material to lime and to reduce the sorbent preparation time. Compared with atmospheric hydration, pressure hydration allows high temperatures (above 100 °C) and high pressure (greater than 1 atm) to increase the silica solubility and enhance the reaction rate. The term "hydration" is used here even though hydrated lime [$Ca(OH)_2$] and not quicklime (CaO) was reacted with a siliceous material. However, as a result of this reaction, the calcium silicate hydrates formed are usually highly hydrated.

Pressure hydration is used commercially to hydrate dolomitic limes (CaO + NgO) since it allows the hydration of MgO, which is difficult to hydrate completely within a reasonable time under atmospheric conditions. At atmospheric pressure, high calcium limes hydrate from within minutes to an hour (Boynton, 1980). Very few dolomitic limes can be substantially hydrated at atmospheric pressure when the

"retention" method is used for periods from 10 to 24 h, permitting only partial hydration of the MgO component of a dolomitic lime. Conditions of high pressure and temperature occurring in the pressure hydrator significantly increase the reaction rate of MgO, so that dolomitic lime can be fully hydrated within time periods typical for high calcium limes. It may be that the use of pressure hydration could also increase the reaction rate of flyash, which was found to be a rate limiting step during the formation of novel flyash-enhanced lime sorbents (Jozewicz and Rochelle, 1985).

The reaction between silica and lime in water media at elevated temperatures has been studied and various forms of calcium silicate hydrates were discovered as the products. Heller and Taylor (1951) studied the hydrothermal reactions of lime and amorphous silica in the temperature range from 110 to 300 °C (230 to 572 °F) for a molar ratio of calcium to silica of 1:1. At 110 °C (230 °F) Type I calcium silicate hydrates (which may vary in composition in the range from $CaO \cdot SiO_2 \cdot nH_2O$ to $3CaO \cdot 2SiO_2 \cdot nH_2O$) appeared to be the final product of reaction. At higher temperatures, they were obtained as an intermediate product. At 135 to 180 °C (275 to 356 °F), $CaO \cdot SiO_2 \cdot H_2O$ was produced, while at 160 to 300 °C (320 to 572 °F) xonolite ($4CaO \cdot 4SiO_2 \cdot O \cdot 2H_2O$) was formed.

In Taylor's study (1964), molar ratios of CaO to SiO_2 varying from 1:2 to 3:1 were investigated for the temperature range of 50 to 1,000 °C (122 to 1,832 °F). At a molar ratio of CaO to SiO_2 of 2:3, gyrolite ($2CaO \cdot 3SiO_2 \cdot 2H_2O$) was formed in the temperature range 140 to 200 °C (284 to 392 °F). With a molar ratio of 2:1, α-$2CaO \cdot SiO_2 \cdot 10H_2O$ (α-dicalcium silicate) was formed instead of gyrolite in the temperature range from 120 to 160 °C (248 to 320 °F). Taylor observed that the hydrates contained molecular water when formed under temperatures up to about 150 °C (302 °F). Above that temperature, they could contain less molecular water but some ionic hydroxyl. Above 300 to 600 °C (572 to 1,112 °F) (depending on the ratio of Ca/Si: lower temperature for the ratio of 2:3, higher for 2:1), the products formed were anhydrous. Some work was done using diatomaceous earth (Kalousek and Prebus, 1958). These researchers reported the formation of Type I calcium silicate hydrates (Ca/Si molar ratio of the product less than 1.5) when lime and diatomaceous earth were pressure hydrated at 175 °C (347 °F) for 2 h with the starting molar ratio of CaO/SiO_2 in the range of 1:1 to 4:3. Note that these studies were conducted under equilibrium conditions and used pure substrates (amorphous silica). During the early

stages of formation of interest in this study (several hours), a mixture of calcium silicate hydrates, with different Ca/Si ratios and varying amounts of water of hydration, is probably formed. The amount of combined moisture in the sorbent is dependent upon the temperature of pressure hydration. The ratio of Ca/Si in the final product depends on the starting weight ratio of siliceous-material-to-lime and on the temperature-dependent availability of active silica.

In order to produce high reactivity sorbents for dry flue gas desulfurization purposes, the product from pressure hydration of silica with lime should have a large surface area and a high moisture (or hydration water) content. The water of hydration, if released on contact with hot flue gas, will provide moisture for enhancing SO_2 absorption. Additionally, releasing the water of hydration can expose more sorbent particle pores and create new surface area for gas/solid reaction.

The results of current pressure hydration tests are discussed in Section 7.

SECTION 3

EXPERIMENTAL PROCEDURES

3.1 APPARATUS

The reactivity of samples was evaluated in a "packed bed reactor" designed to simulate FF operating conditions (Karlsson et al, 1983; Ruiz-Alsop and Rochelle, 1985). The experimental apparatus is shown in Figure 3-1. The packed bed reactor was operated at such high gas velocity (6 cm/s) that the gas film diffusion can be excluded from the overall mass transfer rate controlling step (Jorgensen et al, 1986). The glass reactor (45 mm in diameter, 150 mm in length) was packed with powdered reagent mixed with 70-mesh silica sand to prevent channeling of the sorbent. The sand-to-reagent ratio ranged from 20:1 to 40:1. The reactor was immersed in a water bath controlled at the set temperature to within 0.2 °C. Span gas served as the simulated flue gas, with gas flow monitored by rotameters. Water was metered by a syringe pump, evaporated at about 180 °C (356 °F), and injected into the dry gas to control the humidity. Tubing upstream of the reactor was heat-traced to prevent condensation of the water vapor. Before entering the analyzer, the gas was cooled by an ice bath to condense water vapor. The amount of condensate was measured to check the value of the relative humidity determined using the observed wet and dry-bulb thermometer readings.

The SO_2 concentration measured continuously with an ultraviolet photometric analyzer (Du Pont 411). A bypass of the reactor was provided to allow preconditioning of the bed. Prior to each run, the bed was humidified by passing pure nitrogen for 1 h at the relative humidity at which the experiment was to be performed. Most experiments were performed at a relative humidity of 60 percent, with some experiments at other values in the range of 30 to 80 percent. A relative humidity of 60 percent corresponds to a 10 °C (18 °F) approach to saturation in a spray dryer or fabric filter [30 and 80 percent would correspond to a 21 and 4.4 °C (38 and 8 °F) approach, respectively]. The dry-bulb temperature of the gas through the reactor was controlled at 64.4 °C (148 °F), unless otherwise mentioned. Common

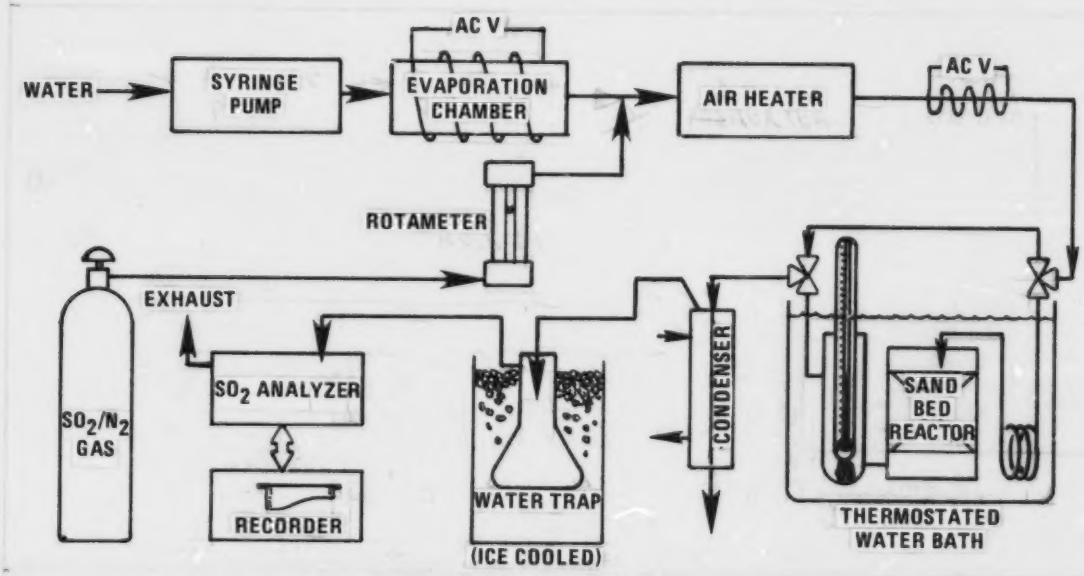


Figure 3-1. Experimental apparatus for testing the reactivity of sorbents.

purity (99.5 percent) nitrogen was used as a conditioning gas at a flow rate of 4.7 L/min (0 °C, 101.3 kPa). The nominal SO_2 concentration was 500 or 1,000 ppm (2,000 ppm occasionally). Exposure time of the sorbent sample to the gas was 1 h.

The reactivity of the new sorbents tested was described by conversion of $Ca(OH)_2$ and SO_2 capture. Conversion of $Ca(OH)_2$ is the number of mol of SO_2 reacted per mol of $Ca(OH)_2$, multiplied by 100 percent. The SO_2 capture is the number of mmol of SO_2 captures per one g of sorbent. While not as informative as conversion, SO_2 capture may be helpful in determining the effect of new sorbent injected into a duct of an already existing particulate control device. The reactivity of reagent grade $Ca(OH)_2$ was established as a baseline. At 60 percent relative humidity and 64 °C (148 °F) in the packed bed reactor, 1 g of regent grade $Ca(OH)_2$ yielded a 17 percent conversion and an SO_2 capture of 2.1 mmol SO_2/g of sorbent after 1 h exposure to 500 ppm SO_2.

3.2 SAMPLE PREPARATION

Sample preparation consisted of two steps: hydration and drying. Hydration took place either in a beaker open to the air (atmospheric hydration) or in a pressure hydrator under controlled conditions of pressure and temperature.

The atmospheric hydration was performed in a beaker which had been heated in a thermostated water bath. Reagents, such as lime and flyash, were mixed with water in the beaker and the resulting slurry was stirred throughout the entire hydration period, which varied from 4 to 24 h. The water bath temperature was usually controlled at 90 °C (194 °F), however 25 and 65 °C (77 and 149 °F) were tried occasionally. After hydration, the slurry was vacuum filtered, and the filter cake produced was microwave dried for 5 min.

Sample preparation also consisted of batch pressure hydration of the siliceous material/lime mixture and drying of the sample. A stainless steel pressure reactor with 300 mL (18.3 in^3) capacity was used as a pressure hydrator. The pressure hydrator was equipped with a stirrer and an electrical heater. Two different methods of pressure hydration were used during this study. In the first method, specified amounts of siliceous material, lime, and water were all placed into the cold reactor. The hydrator was then sealed and heated to the experimental temperature. Twenty minutes usually elapsed before the

hydrator reached the required temperature/pressure levels, making it apparent that this time period would affect the true hydration time, especially for runs with short hydration times (15, 30, 60 min). A second procedure, rapid heating, was therefor adopted (Figure 3-2). Dry siliceous materials and lime (reactants) were placed in the cold pressure hydrator, and the required amount of water was poured into a 300 mL high pressure sampling cylinder. The injection valve in the line connecting the sampling cylinder to the pressure hydrator was closed, and the sampling cylinder was pressurized with nitrogen to about 345 kPa (50 psi) higher than the vapor pressure of water at the experimental temperature. The pressure hydrator was then heated electrically, its temperature controlled by a thermocouple inside the hydrator. When the temperature reached the experimental value, the injection valve was opened and water was instantaneously injected from the sampling cylinder into the hydrator containing the dry reactants and evaporated there. The water injection/evaporation step was monitored by the pressure gauge, and once completed, the injection valve was closed and the sampling cylinder was disconnected. Throughout the hydration period, the sample was vigorously stirred. After completion of the hydration run, the injection valve was opened to depressurize the hydrator via steam release under a ventilated hood. The sample was taken from the reactor and microwave dried for 5 min to ensure its dryness. This method was used for testing the effectiveness of short pressure hydration times.

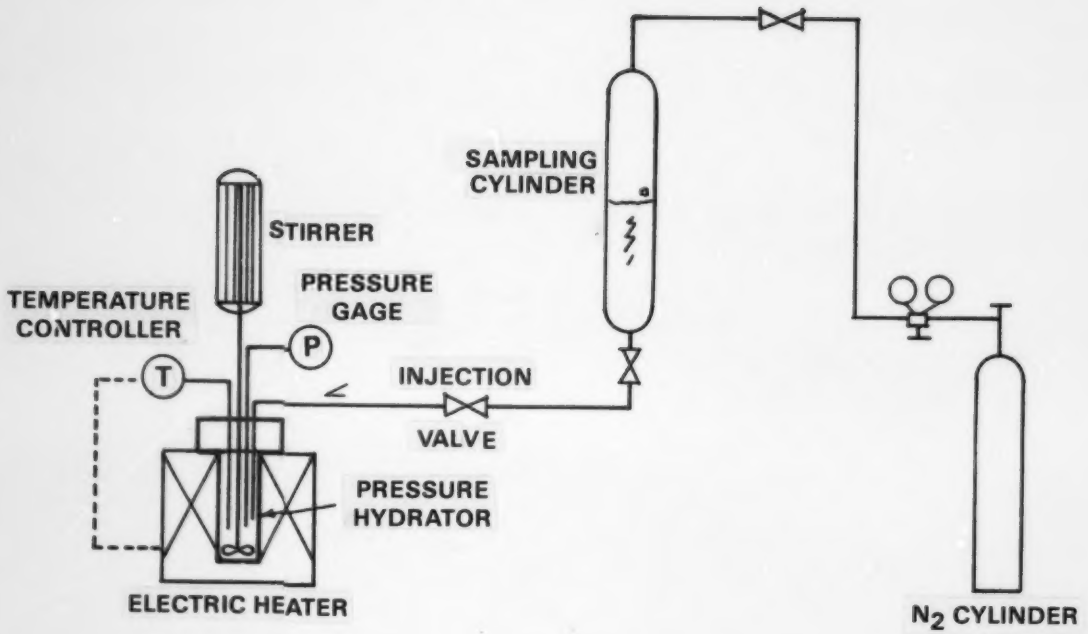


Figure 3-2. Experimental "rapid heating" apparatus for pressure hydration.

SECTION 4

REACTIVATION OF SOLIDS FROM FURNACE INJECTION OF LIMESTONE FOR SO_2 REMOVAL

The objective of this segment of work was to evaluate, on a laboratory-scale, the potential for reactivation and reuse of BLIS to increase overall SO_2 capture and sorbent utilization in both new and retrofitted control applications.

4.1 SAMPLE CHARACTERIZATION

Six different samples of BLIS, produced in 1981 by limestone injection experiments (Blythe, 1982), were received from the DOE. The characterization of these samples is provided in Table 4-1. The available percent of CaO was determined by titration with 0.5 N hydrochloric acid against a phenolphthalein endpoint after the solubilization of $Ca(OH)_2$ with sugar (sugar increased the solubility of $Ca(OH)_2$ via the formation of calcium saccharate). Insoluble solids were determined after 0.5 g of sample was slurried with 200 mL of deionized water and digested with 3 to 5 mL of concentrated HCl. The values of total Ca^{++}, Mg^{++}, and Na^{+} were obtained by atomic absorption, $SO_4^{=}$ by ion chromatography. Particle size analysis was done using a Microtrac analyzer (Leeds & Northrup 7991-01 Particle Size Analyzer). The nitrogen B.E.T. surface area was determined using an Accusorb 2100 form Micrometrics. The characterization of solids from experimental batches of sorbents is provided in Table 4-2.

4.2 UNTREATED BLIS

To evaluate the potential of using untreated BLIS for SO_2 removal downstream of the boiler, the samples were tested using the procedure described earlier. The results showed that virtually no SO_2 removal occurred with the BLIS as received: 3 percent removal in the case of BLIS No. 1 and 5 percent removal in the case of BLIS No. 6. Since the untreated BLIS did not capture SO_2, hydrating the solids at elevated temperature for a prolonged period of time was tried as a means of activating these solids.

Table 4-1. Characterization of BLIS from Hoot Lake Station

BLIS sample number	Mean diameter volume (m)	B.E.T. surface area (m^2/g)	Available[a] CaO (%)	Insoluble solids (%)	Loading[b] (g/g)	$CaSO_4$ (%)	Mg (%)	Na (%)	Total Ca (%)
1	13.5	2.67	14.6	26	1.78	12	6	4	37
2	13.9	1.36	14.0	20	1.43	12	6	4	35
3	12.0	1.48	6.9	29	4.20	12	7	6	33
4	13.5	1.66	20.0	23	1.15	10	4	3	49
5	12.9	1.12	5.5	27	4.91	10	7	4	37
6	16.8	1.74	6.0	35	5.83	10	7	9	40

[a] All percentages are based on weight.
[b] Loading is the ratio of flyash to lime.

Table 4-2. Experimental Results (10 g of BLIS Hydrated with 150 mL H_2O; SO_2 Concentration 500 ppm, Relative Humidity = 60 percent Unless Otherwise Noted)

Experiment No.	BLIS No.	Hydration Temperature (°C)	Mixing Time (h)	B.E.T. Surface Area (m^2/g)	Available $Ca(OH)_2$ (wt%)	SO_2 Capture (mmol SO_2/g)
59	1	65	4	7.95	16.10	1.06
60	1	90	4	18.14	11.80	1.52
63	1	25	4	3.47	15.20	0.46
64	1	90	1	7.19	17.20	1.04
65	1	65	1	4.14	15.40	0.78
66	1	90	8	25.84	8.81	1.94
68	5	65	4	5.66	6.69	0.74
70	6	65	4	12.56	4.86	1.06
72	1	65	8	17.09	16.20	1.79
73	1	25	1	4.53	15.50	3.45
74	1	65	24	24.57	9.70	1.73
76[a]	1	90	4	2.62	11.10	1.68
78	2	65	4	9.42	16.32	1.37
79	3	65	4	4.99	7.28	0.73
80	4	65	4	5.70	20.82	1.01
81	1	25	24	9.29	11.97	1.32
82	1	90	24	50.86	8.14	1.84
83	1	65	4	8.46	15.69	1.24
87	1	65	"0"	4.69	16.21	0.53
88	1	90	"0"	5.57	16.31	0.68
91[a]	1	65	4	16.14	n/a	1.66
92	1	25	16	6.61	13.70	1.22
93	1	45	4	6.55	13.30	0.83
94	1	45	1	5.48	n/a	0.70
95	1	45	8	9.12	14.95	1.45
97	1	25	8	4.73	14.52	0.42
98	1	45	24	19.30	n/a	2.15
100[a]	1	25	4	13.36	11.65	1.33
101[b]	1	65	4	7.95	16.10	0.25
105[a,b]	1	65	4	16.14	n/a	0.27
106[b]	1	90	24	50.86	8.14	0.77
108[c]	1	65	4	7.95	16.10	0.96
109[c]	1	90	24	50.86	8.14	1.84
111	1	25	48	10.92	10.64	1.68
136[a,c]	1	65	4	16.14	n/a	1.72
137[a,c]	1	90	4	22.62	11.10	1.96

a Three weight percent of $(NH_4)_2HPO_4$ was added.
b Relative humidity in the sand bed was 30 percent.
c SO_2 concentration was 1,000 ppm.

4.3 EFFECTS OF HYDRATION

The effect of hydration time/temperature on the reactivity of hydrated BLIS No. 1 is indicated in Figure 4-1. The reactivity is represented by the SO_2 capture, defined as the number of mmol of SO_2 captured by 1 g of sorbent during the 1 h exposure to SO_2 in the packed bed. Figure 4-1 also demonstrates that the SO_2 capture increased with temperature of hydration and was monotonically nondecreasing with hydration time.

For the samples hydrated at 65 and 90 °C (149 and 194 °F) over 1 to 8 h intervals, the SO_2 capture increased with time of hydration but leveled off at about 1.89 mmol SO_2/g after 8 h. Because of the differences in trends for SO_2 capture for hydration at 45 °C (113 °F) and that at 65 and 90 °C (149 and 194 °F), the test for SO_2 capture with BLIS No. 1 hydrated for 24 h at 45 °C (113 °F) was repeated. The earlier result was confirmed; SO_2 capture by BLIS reactivated by hydration over 24 h at 45 °C (113 °F) exceeded that at 65 and 90 °C (149 and 194 °F). While this may be due to the formation of a more active phase at 45 °C (113 °F) than at 65 or 90 °C (149 and 194 °F), no further analytical evidence has been gathered to support this hypothesis. This hypothesis may be evaluated in the future. Hydration times greater than 8 h were needed to activate samples held at 25 °C (77 °F). The SO_2 capture by solids hydrated at this temperature was 0.45 and 0.42 mmol SO_2/g after hydration for 1 and 8 h, respectively.

Two experiments were performed at "zero" time, when water, heated to required temperature, was poured over a dry solid and mixed for about 2 min before vacuum filtering and microwave drying. The SO_2 capture by solids prepared in this way was 0.53 and 0.68 mmol SO_2/g, respectively, when 65 and 90 °C (149 and 194 °F) was used. These results correlate well with those presented by Conoco researchers (Yoon et al, 1985; Fink et al, 1985; Yoon et al, 1985a). Wetting the solid particles, following limestone injection into the boiler, was a prerequisite for significant SO_2 capture, if one assumes that collisions between solid and water particles led to the formation of a moisture layer sufficient to wet the solids in the flue gas duct in the Conoco tests.

The morphology of the hydrated and unhydrated samples was characterized by SEM. In Figure 4-2, a SEM photograph of an unhydrated sample BLIS No. 1, deposits of dead-burned

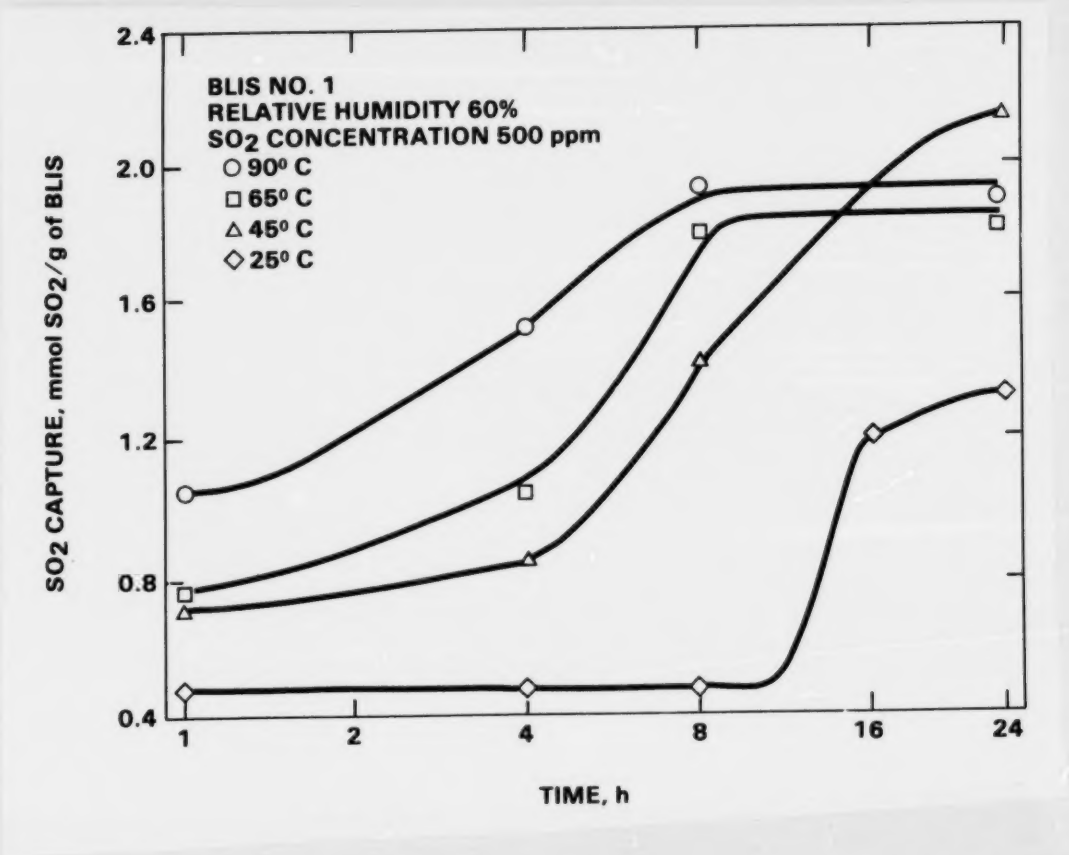


Figure 4-1. The effect of time/temperature conditions of hydration on the SO_2 capture by BLIS in the sand bed (relative humidity = 60 percent, SO_2 concentration = 500 ppm).

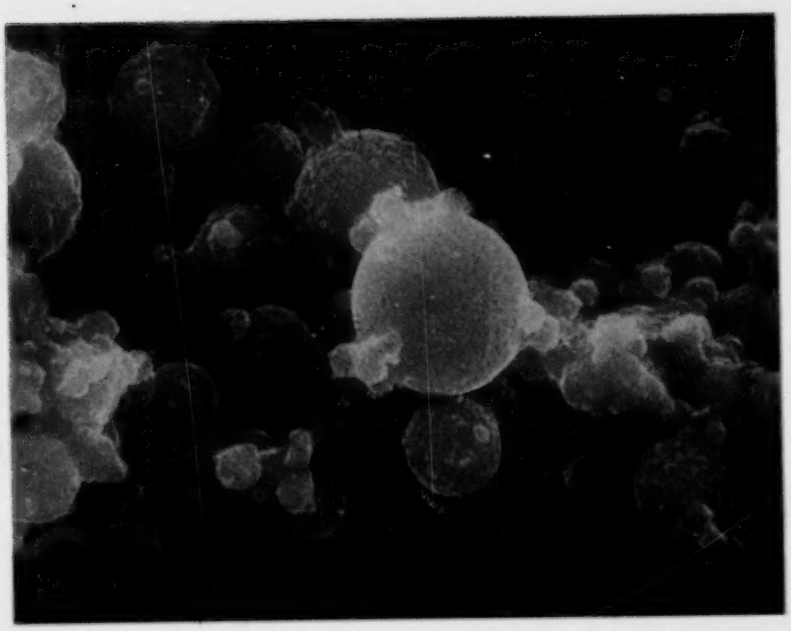


Figure 4-2. SEM photograph of untreated BLIS No. 1 (5,000x).

lime/limestone are evident on the surface of flyash particles. The SEM photograph of a sample of BLIS No. 1, hydrated at 90 °C (194 °F) for 4 h, in Figure 4-3 reveals crystals of a few μm in length, as well as the greatly enhanced surface of flyash particles. X-ray elemental analysis of these "long crystals" gave peaks of Al, S, and Ca, which suggest that these crystals are ettrigite or other synthetic calcium aluminate sulfates. This assumption was later confirmed by x-ray powder diffraction analyses, which detected $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ and/or $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 13H_2O$ [Joint Committee on Powder Diffraction Standards (JCPDS) Numbers 18-275 and 11-197], in the sample hydrated for 4 h at 90 °C (194 °F). Peaks of the same spacing were found in the samples hydrated at 90 °C (194 °F) for 0, 4, and 24 h, but they were not detected in the 1 h hydrated sample. The normalized height of the peak increased from 53, for the 4 h hydrated sample, to 83 for the 24 h sample (height normalized against highest peak). The increase in the intensity (amount) of synthetic calcium aluminate sulfate corresponds to the increase in the B.E.T. surface area and subsequent SO_2 capture in the packed bed reactor. The increased BLIS slurrying time led to greater calcium aluminate sulfate formation and higher SO_2 capture by the corresponding sorbent in the reactor. These peaks were not present in any of the BLIS received from DOE. There was also a strong peak (normalized height of 30) of $Ca(OH)_2$ (JCPDS Number 4-733) in the 1 h hydrated sample, but it was absent in the 24 h sample. Other peaks present in both samples discussed were $CaSO_4$ (JCPDS Number 6-226) and $CaCO_3$ (JCPDS Number 5-586). An ettrigite peak of very high intensity (normalized height of 56) was detected in a sample hydrated at 45 °C (113 °F) for 48 h. In this sample, ettrigite [$3CaO \cdot Al_2O_3 \cdot 31H_2O$] (JCPDS Number 9-416) and limestone ($CaCO_3$) were the only peaks found. Ettringite peaks were found in samples hydrated at 90 °C (194 °F) for "0" and 1 h, but they were absent in samples hydrated at the same temperature for 4 and 24 h. This finding, consistent with observations after all available gypsum in the solution is consumed, suggests that ettrigite decomposes to form other calcium aluminate sulfates (Takemoto and Uchidawa, 1980).

To further increase the SO_2 removal by activated BLIS, ammonium phosphate [$(NH_4)_2HPO_4$] was tested as an additive. The ammonium phosphate was reported to be capable of breaking the glassy layer on the surface of flyash particles so that the dissolution of silica/alumina compounds is facilitated

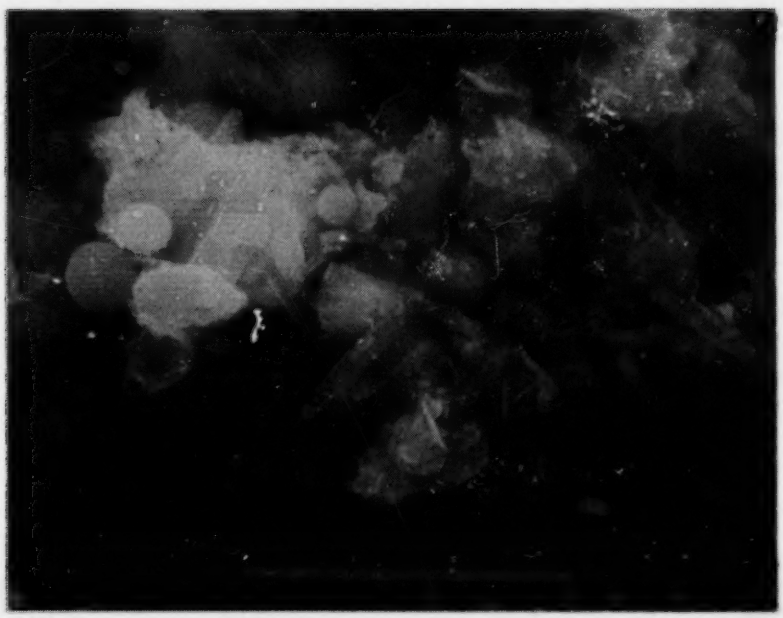


Figure 4-3. SEM photograph of BLIS No. 1 hydrated at 90 °C for 4 h (5,000x).

(Bergeson et al, 1984). It had its most pronounced effect on the reactivity of BLIS hydrated at low temperatures. The addition of 3 percent (by weight) of $(NH_4)_2HPO_4$ tripled the SO_2 capture by the sample hydrated for 4 h at 25 °C (77 °F) from 0.46 to 1.33 mmol SO_2/g BLIS. At 90 °C (194 °F), with all other conditions the same as before, the SO_2 capture increased less dramatically (about 10 percent) from 1.52 to 1.68 mmol SO_2/g BLIS.

4.4 PARAMETRIC TESTS

Parametric tests were also performed to study the effect of flyash loading, SO_2 concentration, and relative humidity on the SO_2 capture by hydrated BLIS. The effect of flyash loading on the SO_2 capture by BLIS hydrated at 65 °C (149 °F) for 4 h is shown in Figure 4-4, which presents SO_2 capture y the $Ca(OH)_2$ component of BLIS as a function of loading. Here loading is defined as the ratio of insoluble solids to available CaO. The CaO and insoluble solids were determined by analyses described earlier. The general trend, as indicated in Figure 4-4, was that SO_2 capture by BLIS increased with higher loading. BLIS No. 3 did not follow this pattern. On the basis of the total sorbent mass, SO_2 capture was about 1 mmol SO_2/g for BLIS No. 1, 2, 4, and 6, and about 0.7 mmol SO_2/g for BLIS Nos. 3 and 5.

Samples from the same sorbent batch used in the packed bed reactor experiments for 500 ppm SO_2 and 60 percent relative humidity were tested at 500 ppm SO_2, and 30 percent relative humidity and 1,000 ppm SO_2 and 60 percent relative humidity. The results in Figure 4-5 present the combined effect of humidity and SO_2 concentration on the SO_2 capture by BLIS No. 1. The general trend suggests that these samples were insensitive to the increase of SO_2 concentration from 500 to 1,000 ppm. However, lowering the relative humidity from 60 percent to 30 percent had a dramatically negative effect on SO_2 capture. Except for the sample hydrated at 90 °C (194 °F) for 24 h (which at 30 percent relative humidity and 500 ppm SO_2 yielded a SO_2 capture of 0.77 mmol SO_2/g of sorbent), the other samples gave much lower SO_2 capture at 30 percent relative humidity than at 60 percent. For example, the SO_2 capture of the sample hydrated for 4 h at 65 °C (149 °F) dropped from 1.06 to 0.25 mmol SO_2/g of sorbent at corresponding conditions. More SO_2 capture data are provided in Table 4-2. The dramatic effect of relative humidity on SO_2 absorption by reactivated BLIS is believed due to its hygroscopic character, with

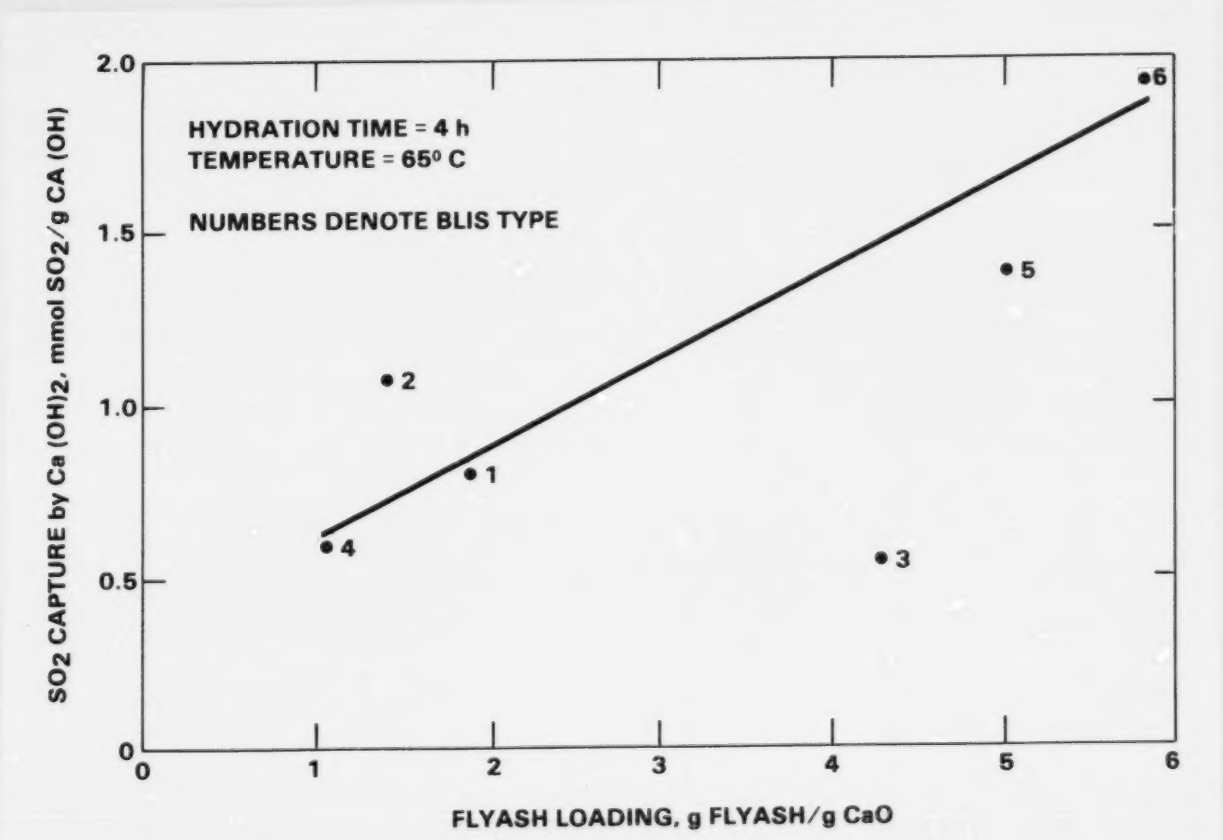
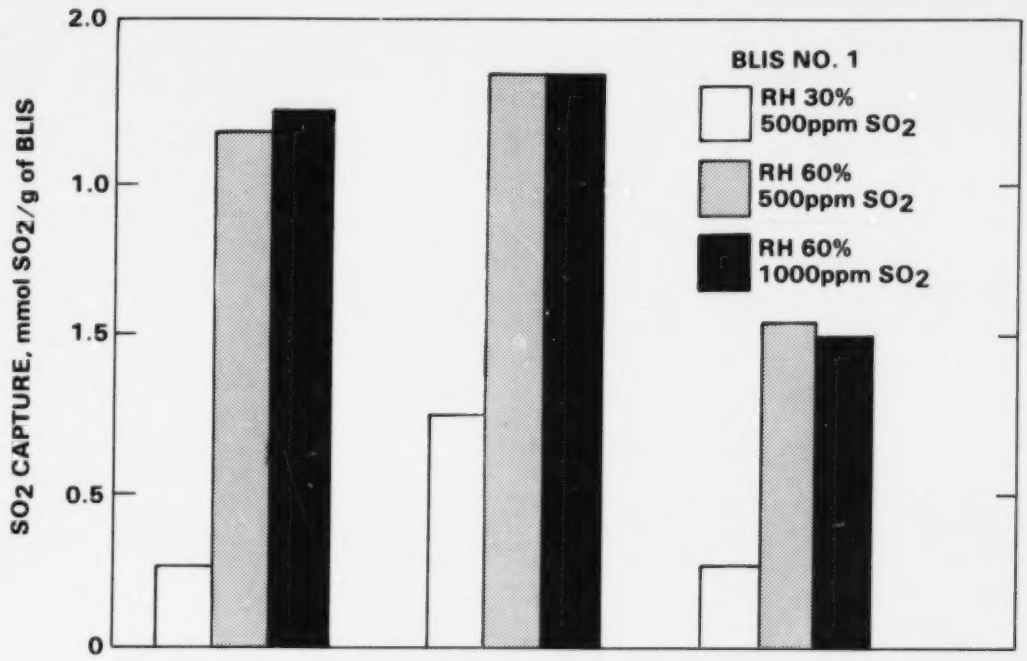


Figure 4-4. The effect of flyash loading on the SO_2 capture by $Ca(OH)_2$ in BLIS (4 h of hydration at 65 °C).



TIME OF HYDRATION, H	4	24	4
TEMPERATURE OF HYDRATION, °C	65	90	65
ADDITIVE, WT. % $(NH_4)HPO_4$	3	0	0

Figure 4-5. Combined effect of conditions of hydration and exposure to SO_2 in the sand bed on the SO_2 capture by BLIS No. 1.

higher humidity increasing sorbent moisture content and enhanced the SO_2/sorbent reaction. Also, at low relative humidity, highly hydrated phases of the sorbent may contract, decreasing the sorbent surface area available for contact with SO_2.

4.5 POSSIBLE MECHANISM OF SO_2 CAPTURE

The data presented earlier indicated that the reactivity of all six different BLIS samples was greatly improved after hydration. The surface area of the atmospherically hydrated samples increased several fold, and highly hydrated crystals were detected using x-ray powder diffraction. During the hydration experiments, the available $Ca(OH)_2$ was tracked. The results (see Figure 4-6) are presented in terms of the B.E.T. surface area as a function of available $Ca(OH)_2$ in the sample after hydration (see also Table 4-2). Initiaily, BLIS No. 1 had 14.6 percent $Ca(OH)_2$ available and a surface area of 2.67 m^2/g. As the surface area of the hydrated BLIS increased via treatment, the available $Ca(OH)_2$ decreased. This decrease is explained by the $Ca(OH)_2$ combined with silica being digested from the BLIS and forming calcium silicates which cannot be detected by the analysis for available $Ca(OH)_2$.

A significant change in surface area was evident when BLIS No. 1 was hydrated under different time/temperature conditions. The initial value for untreated BLIS No. 1 was 2.67 m^2/g, but the maximum surface area measured was 50.86 m^2/g after 24 h of sample hydration at 90 °C (194 °F). The surface area increased with both hydration time and temperature. For example, after 8 h of hydration it was 4.73 m^2/g for 25 °C (77 °F) and 25.84 m^2/g for 90 °C (194 °F). Increasing the hydration time from 4 to 24 h at 65 °C resulted in the surface area growing from 6.95 to 24.57 m^2/g. The good correlation between the developed surface area and SO_2 capture by the sample is evident in Figure 4-7 for BLIS No. 1. Samples hydrated for 4 h with 1 or 3 percent (by weight) of $(NH_4)_2HPO_4$ gained reactivity (following significant increases in surface area) in a much shorter time than those hydrated without the additive (see also Table 4-2).

The beneficial effect of increased surface area on the conversion of SO_2 is dependent on the rate limiting step. If SO_2 removal is controlled by the diffusion of SO_2 through the "ash" layer, increased surface area provides more gas-solid contact and, therefore, the "ash" formed in the initial steps of the reaction is spread over a larger surface in a thinner layer. If SO2 removal is controlled by the chemical

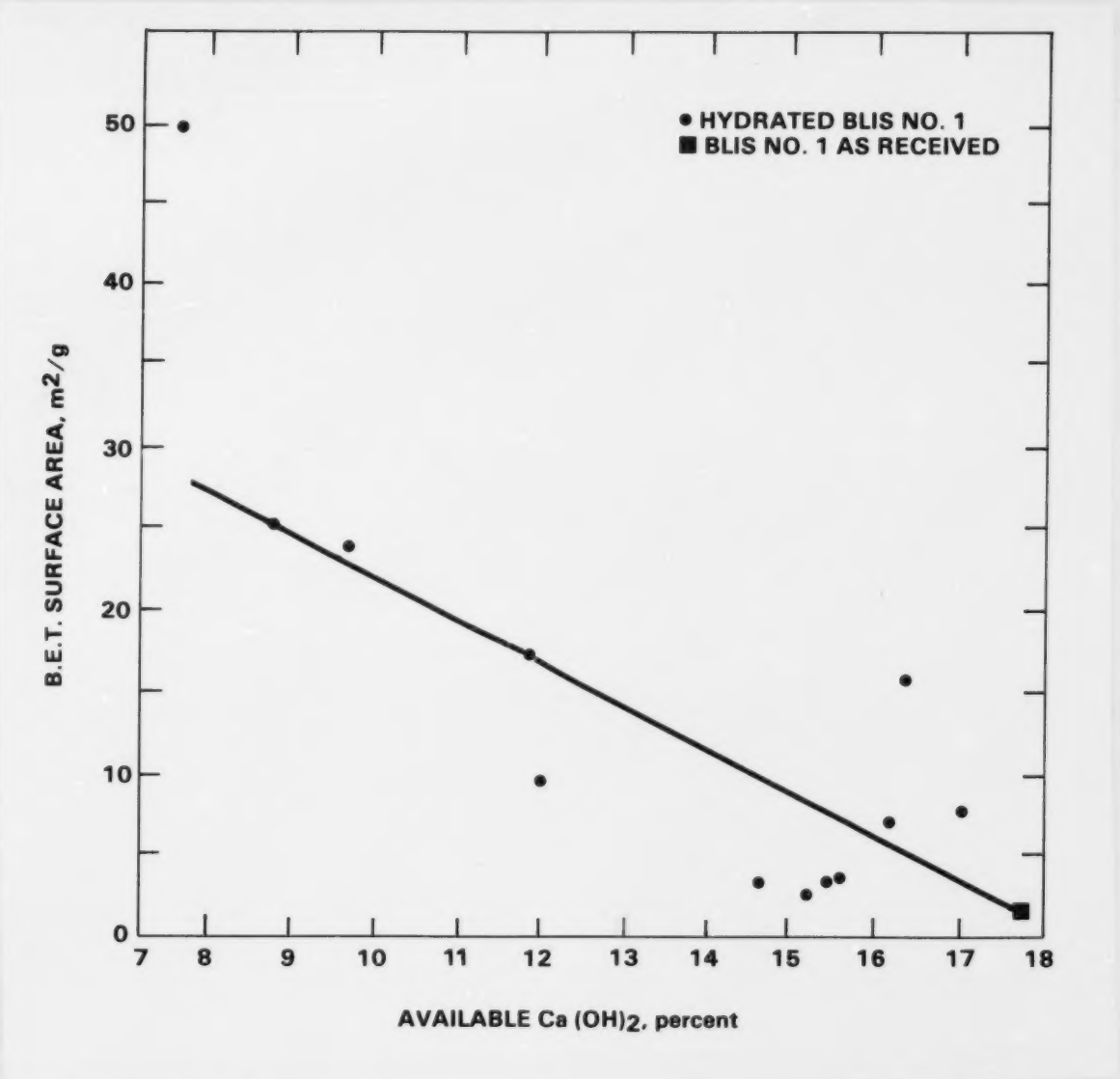


Figure 4-6. Effect of hydration on the properties of solids (BLIS No. 1) hydrated under different time/temperature conditions.

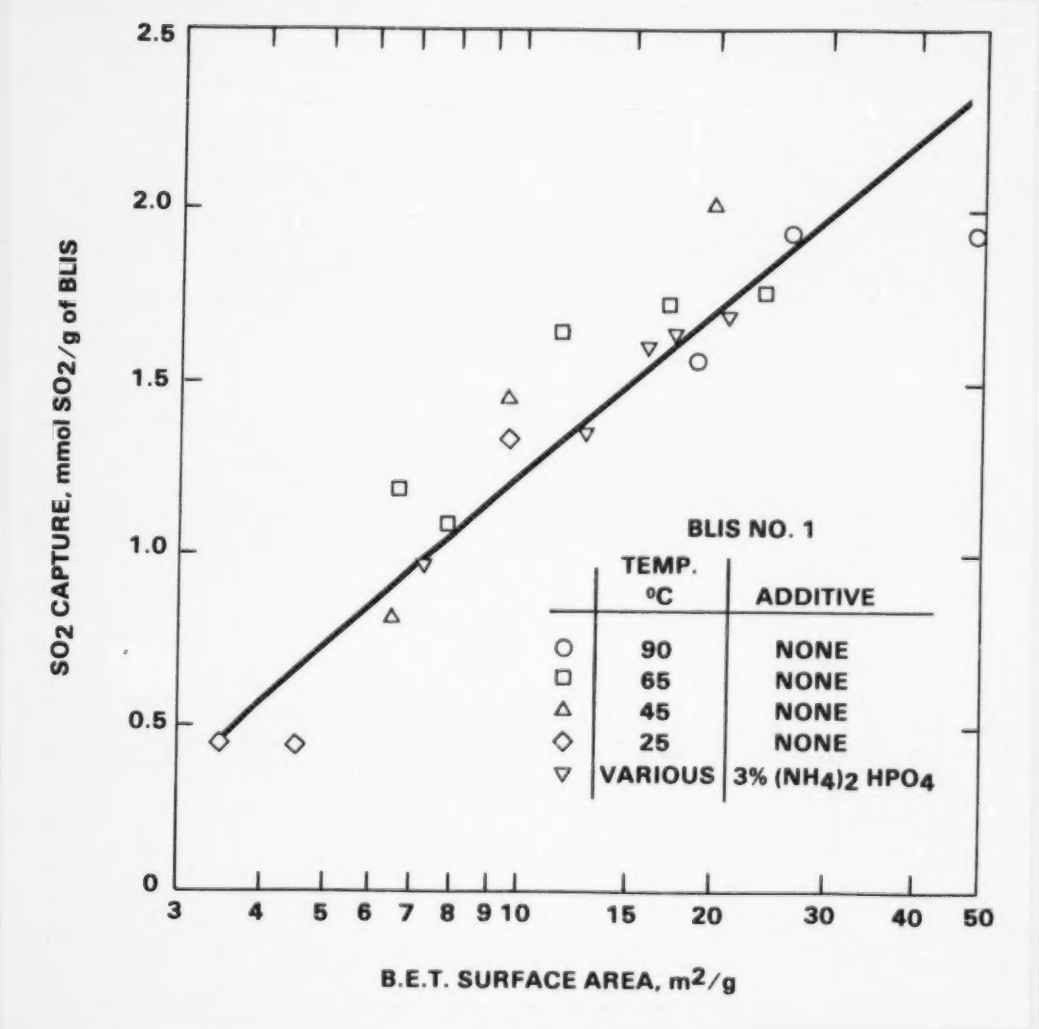


Figure 4-7. Correlation between the surface area developed during hydration and SO_2 capture by BLIS No. 1 in the sand bed.

reaction, the reactivity could also increase with higher sorbent surface area. More importantly, when the sorbent surface contains highly hydrated species, the water of hydration can be released upon contact with hot gas. This release provides moisture which may be necessary for SO2 capture by Ca(OH)2. Releasing the water of hydration could expose more pores, therefore creating new surface areas.

4.6 POTENTIAL APPLICATION

The reactivated sorbents developed and studied in the bench-scale experiments reported here may make dry sorbent injection an attractive low cost SO_2 control option. While the test procedure used appears more appropriate to dry sorbent injection into a duct carrying low temperature flue gas followed by particulate collection in a baghouse, spray drying with the sorbent in slurry form and particulate collection via a baghouse or an electrostatic precipitator may also be technically and economically feasible. However, as shown by limited in-house pilot plant testing on flyash/lime sorbents, the hygroscopic nature of these sorbents limited the approach to saturation temperature to values somewhat above the minimum 10 °C used in lime spray drying for SO_2 control. These values are more suited for acid gas control in municipal waste incinerators. Pilot plant testing also determined that spray drying of the activated flyash/lime sorbents produced a less reactive product, with larger particles and lower B.E.T. surface area, than did vacuum filtering followed by oven or microwave drying. A similar behavior would be expected of reactivated BLIS. Further work is needed to evaluate reactivated BLIS and other advanced sorbents now being developed for spray drying application, as well as determining their technical and economic feasibilities at the pilot and demonstration scales.

4.7 CONCLUSIONS

From this study, the following conclusions may be drawn:

1. Reactivity of BLIS samples is possible and may be accomplished by atmospheric hydration under conditions permitting the reaction of calcium with silica to form high surface area sorbents.
2. New crystals ($CaO \cdot Al_2O_3 \cdot CaSO_4$ compounds) were found in hydrated BLIS samples.
3. The amount of available $Ca(OH)_2$ detected by analysis of the hydrated BLIS samples decreased as the B.E.T. surface area of the sorbent and its SO_2 capture increase.

4. The surface area of hydrated BLIS samples increases with hydration time and temperature; SO_2 capture correlates well with surface area, increasing with increasing surface area.
5. The SO_2 capture of the hydrated BLIS samples increases with an increasing ratio of flyash to lime in the sorbent.
6. The reactivity of hydrated BLIS samples is very sensitive to the relative humidity of the test gas, with SO_2 capture being enhanced by high relative humidity.
7. Early pozzolanic reactions in the hydrated BLIS samples are probably responsible for the formation of a highly reactive sorbent for SO_2 removal.
8. A potential mechanism for enhancing SO_2 capture involves increasing particle surface area of the reactivated BLIS. This increased surface area, and possible additional area exposed when water evaporates from the particle pores by contacting the hot gas, appears to be the basis for the enhanced reactivity of the reactivated solids.

SECTION 5

SCREENING OF ALTERNATE SOURCES OF SILICA

The most obvious and abundant source of silica in power plants is flyash generated from the combustion of coal. Table 5-1 indicates that the two types of flyashes tested during the current work contain a minimum of 50 percent silica. The pozzolanic reaction between lime and silica in the presence of water can generate calcium aluminum silicate hydrates. These hydrates are responsible for the high reactivity reported (Jozewicz and Rochelle, 1985). However, the pozzolanic reaction rate between flyash and lime is usually limited by the dissolution rate of the glassy layer on the flyash particle surface. Long reaction times and high temperatures are required to complete the reaction. It is obvious that siliceous materials from sources other than flyash can also be used for pozzolanic reaction with lime. This section describes the bench-scale evaluation of alternate sources of silica, including cryptocrystalline forms of silica and aluminosiliceous clays.

5.1 CRYPTOCRYSTALLINE SILICA

Among cryptocrystalline silica materials tested were diatomaceous earths, tripolis, and pumices. The samples were donated by vendors, and their properties are listed in Table 5-2. Three different kinds of diatomaceous earths were tested—natural, calcined, and flux calcined. Three samples from Manville, Inc., originating from the same deposit, were supposedly of the same composition, but differed significantly in B.E.T. surface area. Flux calcined White Mist had a surface area of only 3 m^2/g, while natural diatomaceous earth usually has surface area in the range 40 to 50 m^2/g. Sodium-based additives used during calcination caused sintering at the high temperatures [900 °C (1,652 °F)] in the kiln, and produced siliceous slag on the surface of diatomaceous earth similar to the glass layer on the surface of flyash particles. Two kinds of tripoli, differing in composition, and several grades of pumice were tested.

Table 5-1. Typical Flyash Sample Analytical Results

Flyash	Clinch River	San Miguel
CaO	5.2	5.4
SiO_2	51.6	64.9
Al_2O_3	24.7	20.3
Na_2O	0.5	2.8
MgO	1.8	0.7
K_2O	3.3	2.2
Fe_2O	7.8	3.7
TiO_2	1.4	—
Others (SO_3, CO_2...)	3.7	—

(all numbers in weight percent)

Table 5-2. Physical/Chemical Properties of Tested Cryptocrystalline Silica

Trade Name	Mineral	Vendor	B.E.T. Surface Area (m^2/g)	Composition Weight Percent CaO	SiO_2	Al_2O_3	Other
Kenite 108	Natural diatomaceous earth	Witco Chemical Corporation	3.5-4.0	n/a	n/a	na/	SiO_2 dust
MN-53	Natural diatomaceous earth	Eagle-Picher Industries, Inc.	40	0.9	83.7	5.6	Water absorbtion 150 lb/100 lb
MP-78	Calcined diatomaceous earth	Eagle-Picher Industries, Inc.	n/a[a]	0.2	90.0	6.5	
Infusorial Earth	Calcined	Fisher Scientific	n/a	n/a	n/a	n/a	Fisher No. 122
Celite White Mist	Flux calcined diatomaceous earth	Manville Products Corp.	2[b]	0.3	93	2	2% Na_2O
Standard Super-Cel	Calcined diatomaceous earth	Manville Products Corp.	n/a	0.5	91	2	About 10% cristobalite
Celite Filter-Cel	Natural diatomaceous earth	Manville Products Corp.	20	0.5	87	3	Less than 3% quartz
Rose Tripoli	Tripoli	Charles B. Chrystal Company	n/a	none	94.4	2.7	94% passing 200 mesh

(continued)

Table 5-2. Physical/Chemical Properties of Tested Cryptocrystalline Silica (concluded)

Trade Name	Mineral	Vendor	B.E.T. Surface Area (m^2/g)	Composition Weight Percent CaO	SiO_2	Al_2O_3	Other
Cream Tripoli	Tripoli	Charles B. Chrystal Company	n/a	none	97.5	0.65	
FF Vulcan	Pumice	Charles B. Chrystal Company	n/a	trace	72.0	12.5	8% K_2O and Na^{20}
FFFF Vulcan	Pumice	Chas. F. Hommedieu Incorporated & Sons	n/a	n/a	n/a	n/a	
Empire White	Pumice	Empire White Products, Inc.	n/a	n/a	n/a	n/a	95% passing 325 mesh
Hess Pumice	Pumice	Hess Pumice Products	n/a	0.8	70	14.2	90% passing

[a] n/a means not available.
[b] Measured on-site.

A screening series of experiments was performed on the samples hydrated at 90 °C for 4 h. The ratio of siliceous material to CaO was 1:1. Conditions in the packed bed reactor were 60 percent relative humidity, 64.4 °C (148 °F) temperature, and an SO2 concentration of 1,000 ppm. The results of screening tests are shown in Figure 5-1. The broken line in Figure 5-1 represents the reactivity of reagent grade $Ca(OH)_2$. The three natural grades of natural diatomaceous earth (MN-53, Kenite, and Filter Cel) clearly performed better than calcined materials. Flux calcined White Mist yielded the poorest performance. To test the idea that calcination and the addition of sodium salts have an adverse effect on the reactivity of sorbents, diatomaceous earth which produced the most reactive sorbents was calcined for 4 h at 900 °C (1,652 °F) and later hydrated with CaO, using standard procedures. Calcination caused a decrease in the B.E.T. surface area from 56 to 11 m^2/g. The hydrated sorbent produced from calcined diatomaceous earth yielded a $Ca(OH)_2$ conversion of 48 percent (SO_2 capture of 3.22 mmol SO2/g of sorbent). When natural MN-53 was calcined with 10 weight percent NaCl at 900 °C (1,652 °F) for 4 h and later hydrated using standard procedures, the resulting sorbent yielded a 29 percent conversion of CaO (1.94 mmol SO_2/g of sorbent SO_2 capture). A general view of diatomaceous earth MN-53 is shown in Figure 5-2, and details illustrating extremely well developed surface area are provided in Figures 5-3 through 5-5. Reagent grade diatomaceous earth (washed and calcined) is presented in Figure 5-6.

Several grades of pumice and two grades of tripoli were tested for possible removal of SO_2 after hydration with CaO. The reactivities of these prepared sorbents, tested under the same conditions as described for diatomaceous earth, are presented in Figure 5-7. All performed poorly, and some reactivities were even lower than that of reagent grade $Ca(OH)_2$.

5.2 CLAYS

Several grades of naturally occurring bentonitic clays were hydrated with lime and tested in the packed bed reactor for their reactivity. Clays of Filtrol grade were acid activated and "tailored" for a specific use. The properties of the clays which were used are listed in Table 5-3, and performance of sorbents produced from those clays is given in Figure 5-8. All sorbents were prepared and tested under normal conditions described in Section 5.1. As can be seen from Figure 5-8, all clays yielded sorbents of higher reactivity that did reagent grade $Ca(OH)_2$ (shown as a broken line in Figure 5-8). The most

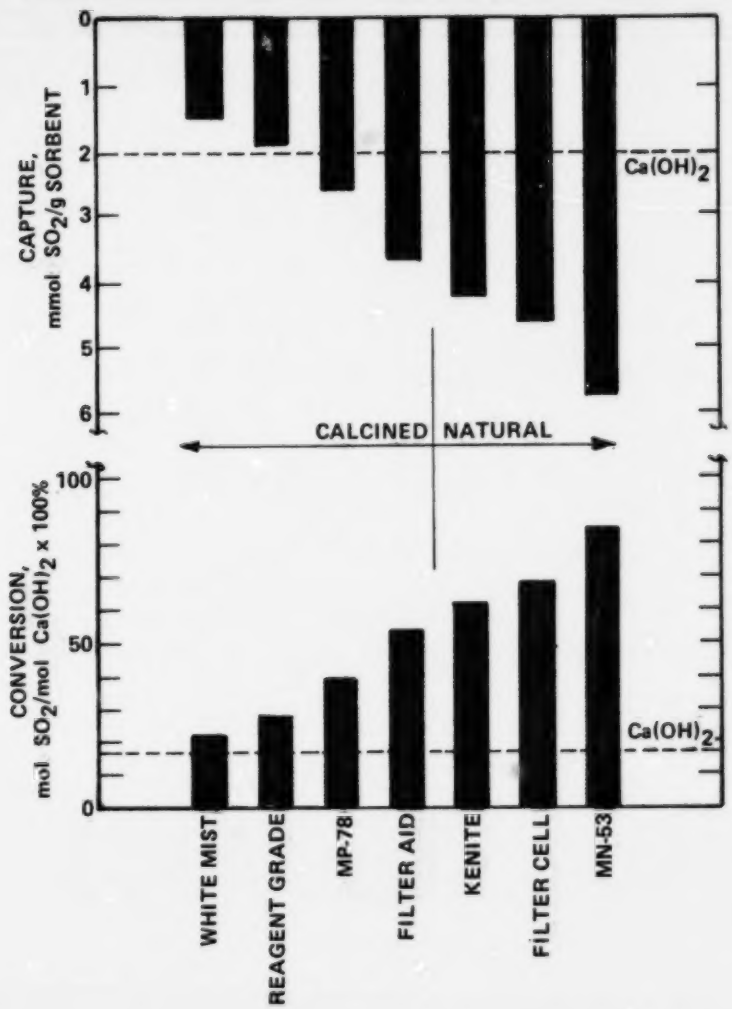


Figure 5-1. Evaluation of diatomaceous earth-based sorbents for SO_2 removal (conditions for the sand-bed reactor: 60 percent relative humidity, 64.4 °C (148 °F) temperature, and 1,000 ppm SO_2 concentration).

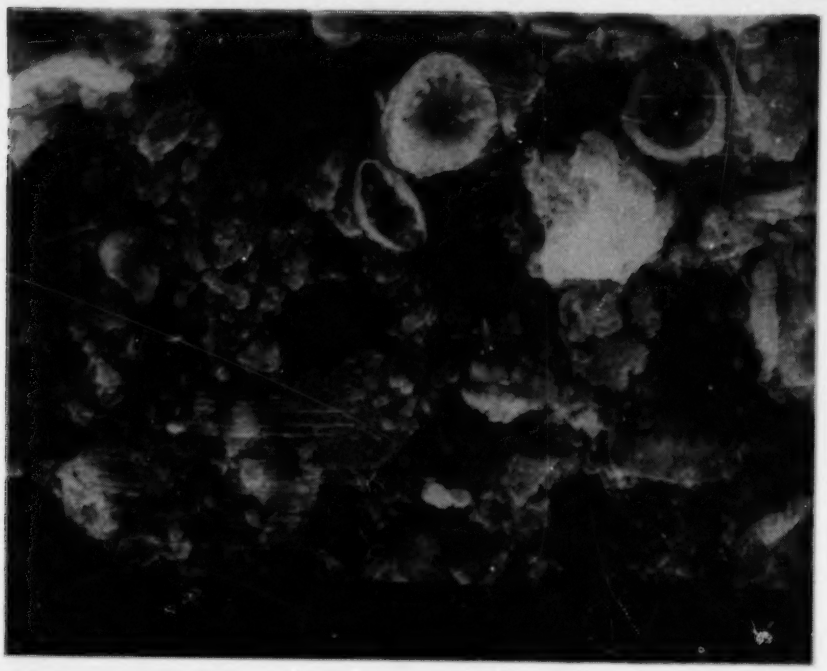


Figure 5-2. SEM photograph of MN-53, general view (2,000x).

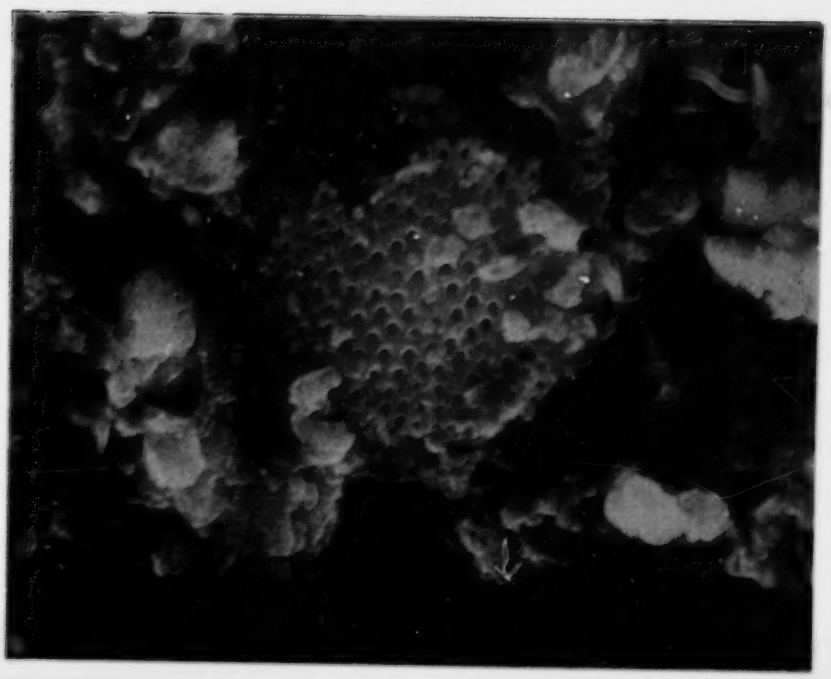


Figure 5-3. SEM photograph of MN-53, detail (5,000x).

Figure 5-4. SEM Photograph of MN-53, detail (5,000x).

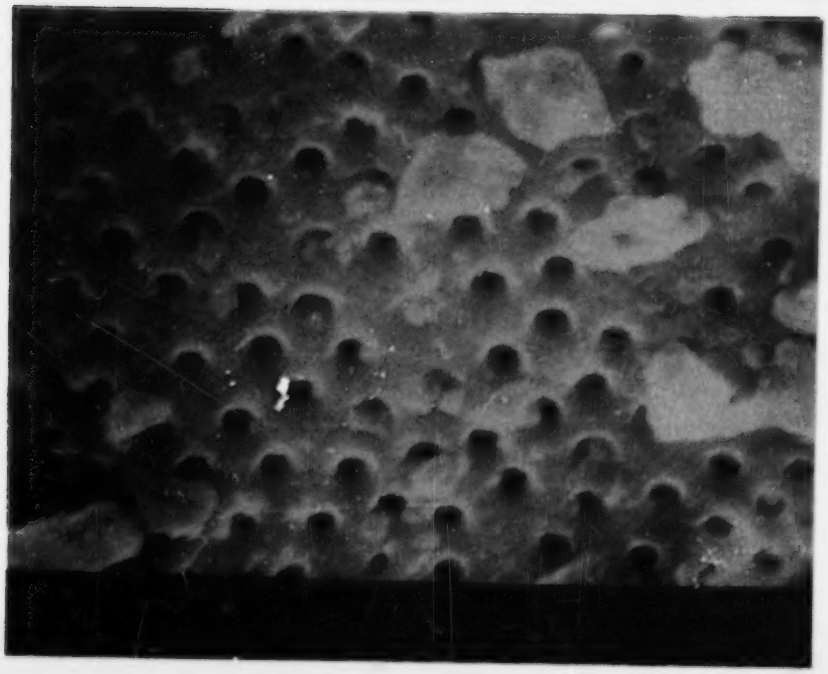


Figure 5-5. SEM photograph of MN-53, detail (20,000x).

Figure 5-6. SEM photograph of a reagent grade (washed, calcined) diatomaceous earth (5,000x).

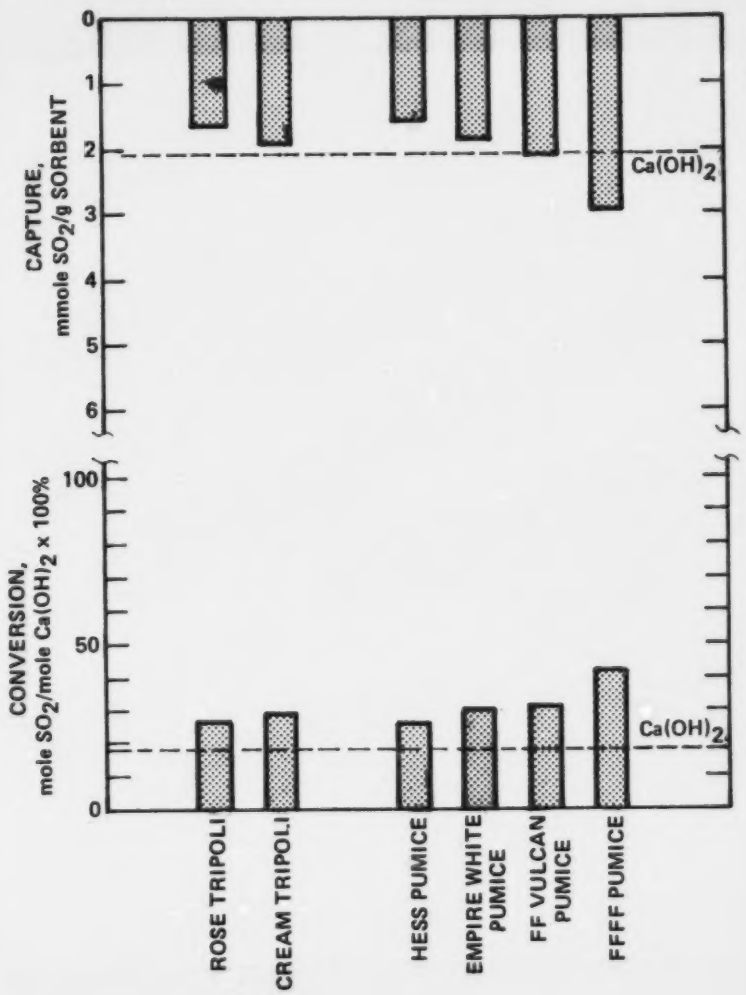


Figure 5-7. Evaluation of pumice- and tripoli-based sorbents for SO_2 removal (conditions for the sand-bed reactor the same as in Figure 5-1).

Table 5-3. Physical/Chemical Properties of Tested Bentonitic Clays

Trade Name	Mineral	Vendor	B.E.T. Surface Area (m^2/g)	Composition weight % CaO	SiO_2	Al_2O_3	Other
149 Bentonite	Montmorillonite	Whittaker, Clark & Daniels, Inc.	n/a	0.1-1	58-64	18-21	96% less than 40 m
660 Bentonite	Montmorillonite	Whittaker Clark & Daniels, Inc.	n/a	0.1-1	58-64	18-21	100% less than 20 m
Volclay 325	Na-Montmorillonite	American Colloid Company	n/a	0.65	63.0	21.1	Volcanic origin
Bentonite	Montmorillonite	Fisher Scientific Company	n/a	n/a	n/a	n/a	Powder, Fisher No. B235
Western Bentonite	Montmorillonite	Whitehead Brothers Co.	n/a	0.5	55-57	20.1	Volcanic origin
Southern Bentonite	Ca-Montmorillonite	Whitehead Brothers Co.	n/a	1.2-3.5	56-59	18-21	
Filtrol 1	Montmorillonite	Harshaw/Filtrol	275	a	b	c	70% passing 325 mesh
Filtrol 4	Montmorillonite	Harshaw/Filtrol	280	a	b	c	75% passing 325 mesh
Filtrol 13	Montmorillonite	Harshaw/Filtrol	300	a	b	c	78% passing 325 mesh
Filtrol 20	Montmorillonite	Harshaw/Filtrol	295	a	b	c	76% passing 325 mesh

(continued)

Table 5-3. Physical/Chemical Properties of Tested Bentonitic Clays (concluded)

Trade Name	Mineral	Vendor	B.E.T. Surface Area (m^2/g)	Composition weight % CaO	SiO_2	Al_2O_3	Other
Filtrol 105	Montmorillonite	Harshaw/Filtrol	330	a	b	c	80% passing 325 mesh
	Hectorite	Ward's Natural Science Establishment	n/a	n/a	n/a	n/a	from Hector, CA
	Na-Montmorillonite	Ward's Natural Science Establishment	n/a	n/a	n/a	n/a	from Clay Spur, WY
	Na-Ca-Montmorillonite	Ward's Natural Science Establishment	n/a	n/a	n/a	n/a	Beidellite from Cameron, AZ

n/a not available
[a] Between 0.1-1% CaO
[b] Between 55-70% SiO_2
[c] Between 18-25% Al_2O_3

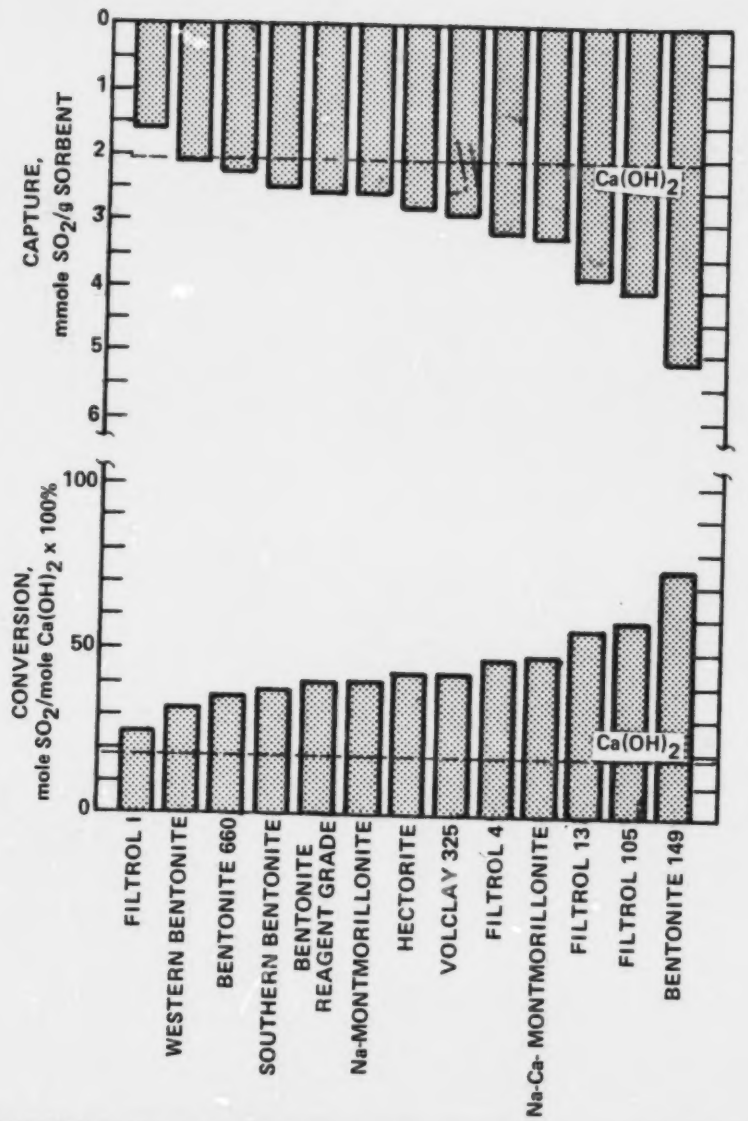


Figure 5-8. Evaluation of bentonitic clay-based sorbents for SO_2 removal (conditions for the sand-bed reactor the same as in Figure 5-1).

effective of this group, Bentonite 149, yielded a $Ca(OH)_2$ conversion of 76 percent and an SO_2 capture at 5.14 mmol SO_2/g of sorbent.

Bentonitic clay of volcanic origin, Volclay 325, yielded an intermediate conversion of 43 percent and SO_2 capture at 2.88 mmol SO_2/g of sorbent. The sample of Volclay 325 is shown in Figure 5-9. Particles about 5 μm in diameter, with well developed surface area, can be seen.

Several kaolins were also hydrated with lime and tested in the packed bed reactor. Most of the sorbents prepared from kaolins performed more poorly than those prepared from bentaonitic clays. The best kaolin, ASP-400 from Engelhard, yielded a $Ca(OH)_2$ conversion of 54 percent and an SO_2 capture of 3.67 mmol SO_2/g of sorbent. The properties of the kaolins tested are listed in Table 5-4. The performance of kaolin-based sorbents, at base conditions of hydration and exposure to SO_2, is presented in Figure 5-10. A general view of ASP-400 is provided in Figure 5-11, in which agglomerates of small particles (several μm) can be seen.

5.3 MISCELLANEOUS MATERIALS

Figure 5-12 presents the results of the initial screening of miscellaneous materials for their SO_2 removal potential in the packed bed reactor. Two kinds of micas, vermiculite and illite-bearing shale, yielded $Ca(OH)_2$ conversions of about 30 percent. Also tested was a sample of Soil C from Ward's Natural Science Establishment (terra rosa, about 40 percent SiO_2). The ocean beach sand tested at base conditions yielded 30 percent $Ca(OH)_2$ conversion and an SO_2 capture of 2.30 mmol SO_2/g of sorbent. However, at 5 weight percent of beach sand, the $Ca(OH)_2$ conversion was 38 percent and SO_2 capture was as high as 3.95 mmol SO_2/g of sorbent. Detailed results of experiments with ocean sand from the vicinity of North Myrtle Beach, SC are provided in Table 5-5. It is still unclear as to what the enhancement mechanism was in the case of ocean sand. As shown before, sand has very poor dissolution and therefore should not yield silica for the formation of calcium silicates. It may be that crustaceous materials, finely ground by the tidal motions of ocean water, dissolve under laboratory conditions and provide a source of reactive calcium or silicate.

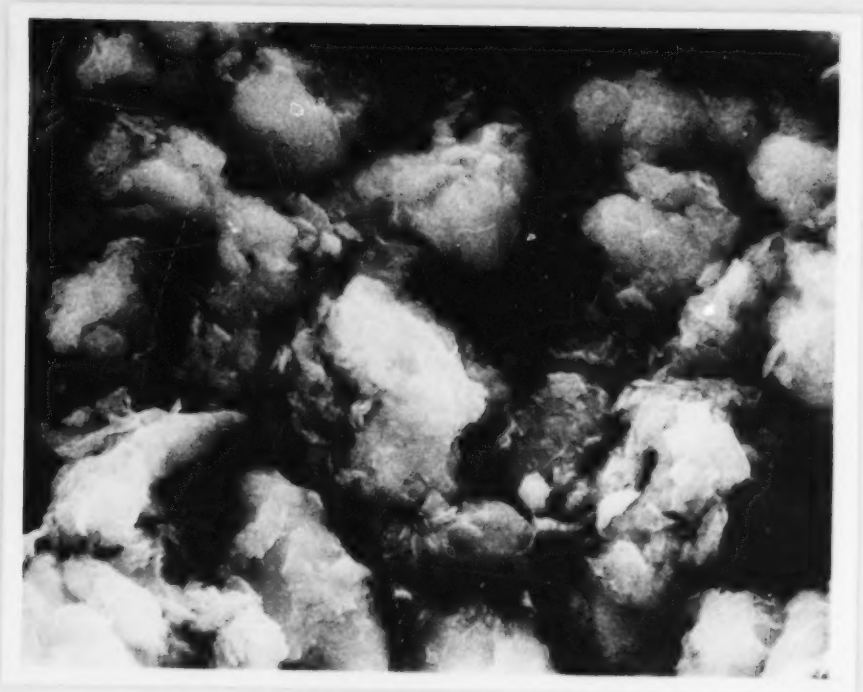


Figure 5-9. SEM photograph of Volclay 325 (5,000x).

Table 5-4. Physical/Chemical Properties of Tested Kaolins

Trade Name	Mineral	Vendor	Average Particle Size (m)	Composition weight% CaO	SiO_2	Al_2O_3	Other
Burgess No. 17	Aluminum Silicate	Burgess Pigment	0.5	n/a	45.0	38-40.0	pH=7.0
Burgess No. 80	Aluminum Silicate	Burgess Pigment	0.5	n/a	45.0	38-40.0	pH=4.6
Burgess No. 97	Aluminum Silicate	Burgess Pigment	0.2	n/a	45.0	38-40.0	pH=7.0
ASP 400	Aluminum Silicate	Engelhard Corporation	4.8	0.03	45.4	38.5	Free Moisture 1.0% max
Kaolin Regent Grade	n/a	Fisher Scientific Company	n/a	n/a	n/a	n/a	Colloidal Fisher No. K6
——	Kaolinite	Ward's Natural Science Establishment	n/a	n/a	n/a	n/a	From Mesa Alta, NM
King's Mountain Clay	Kaolinte	King's Mountain Mica Company, Inc.	14	trace	45	35	68% Kaolinite 14% Mica 13% Feldspar
RC-32	Kaolinite	Thiele Kaolin Company	n/a	n/a	n/a	n/a	Air floated
Acidic Clay	Kaolinite	Unimin, Inc.	n/a	n/a	n/a	n/a	Acid washed
Kaolin	Kaolinite	Unimin, Inc.	n/a	n/a	n/a	n/a	$CaCl_2$ washed

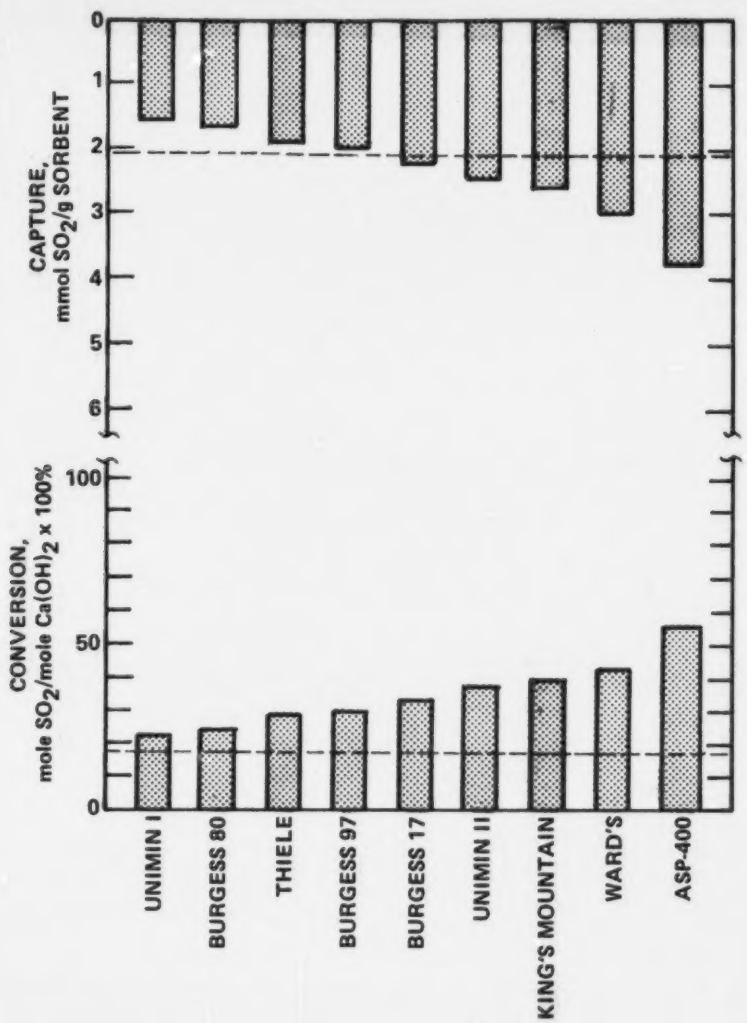


Figure 5-10. Evaluation of kaolin-based sorbents for SO_2 removal (conditions in the sand-bed reactor the same as in Figure 5-1).

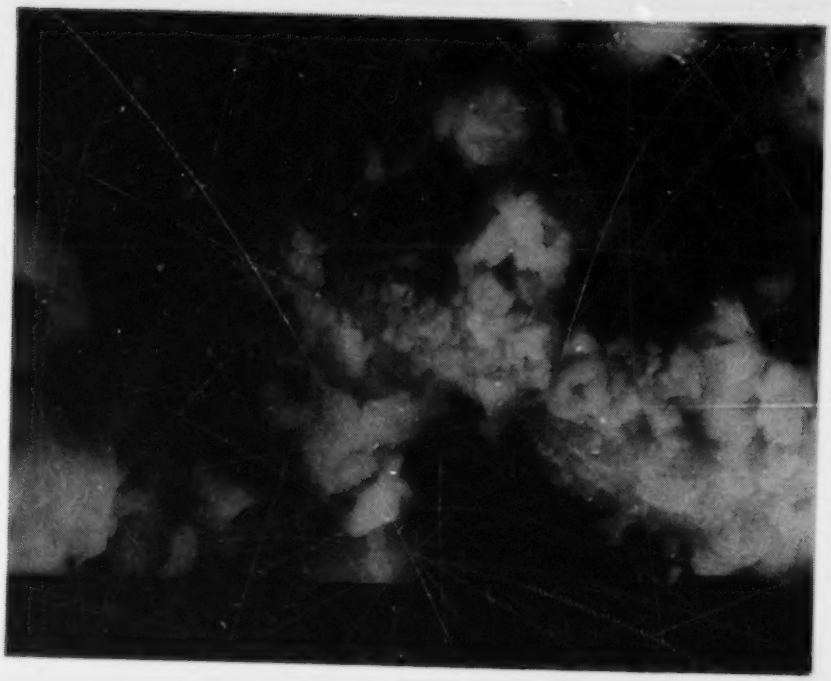


Figure 5-11. SEM photograph of ASP-400 kaolin clay (2,000x).

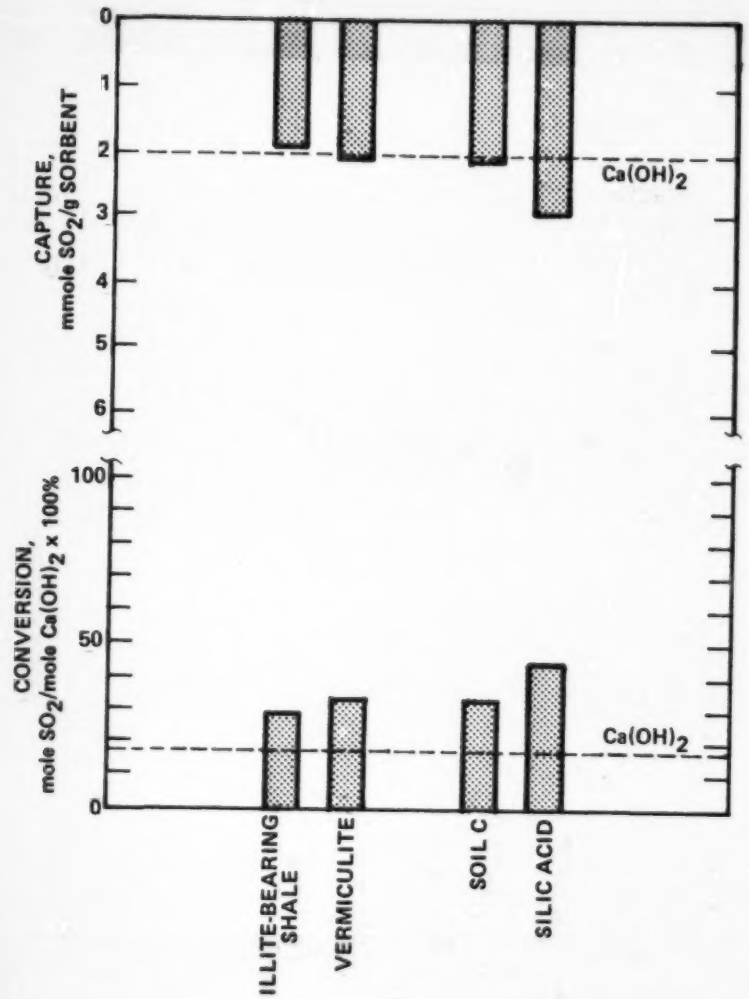


Figure 5-12. Evaluation of miscellaneous materials-based sorbents for SO_2 removal (conditions in the sand-bed reactor the same as in Figure 5-1).

Table 5-5. Results of Experiments With CaO/Ocean Beach Sand Sorbents

Promoter Weight Percent (%)	Amount of CaO (g)	Amount of Sand[a] (g)	Conversion[b] (%)	SO_2 Capture[b] (mmol/g)
5	9.5	0.5	30	3.73
10	9	1	29	3.51
22	7	2	29	2.47
50	5	5	29	2.30

a Ocean beach sand from vicinity of North Myrtle Beach, SC
b After 1 h in the sand bed reactor. Experimental conditions in the sand bed reactor: 60 percent relative humidity, 64.4 °C (148 °F) temperature, and 1,000 ppm SO_2 concentration.

5.4 PARAMETRIC TESTS

MN-53 (diatomaceous earth) and Bentonite 149 (bentonitic clay) were identified as the most reactive siliceous materials and subsequently were selected, with several other promoters, for parametric tests. At first, the effect of the silica concentration (weight percent) was investigated, and the results are shown in Figure 5-13. As can be seen, both conversion and SO_2 capture for MN-53 and Bentonite 149-based sorbents peaked at 50 percent weight of the silica, corresponding to a silica/CaO ratio of 1.

One possible explanation of the SO_2 capture versus weight percent phenomenon is that calcium silicate was formed according to the following hypothetical reaction:

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 \cdot H_2O \qquad (5.1)$$

Now, if it is assumed that the relative abilities to capture SO_2 decrease in the order: $CaSiO_3 \cdot H_2O > Ca(OH)_2 > SiO_2$, then only at equimolar conditions can the greatest amount of the most effective SO_2-capture material be produced. At $Ca(OH)_2/SiO_2$ ratios both greater than and smaller than unity, the SO_2 removal capability would fall off, and more dramatically for the case of excess SiO_2 since it is essentially unreactive to SO_2. This assumption is illustrated in Figure 5-14, where CH represents $Ca(OH)_2$ and S represents SiO_2. Thus the SO_2 capture ability of the product mix would decrease in the order of Case 1 > Case 2 > Case 3, given the assumption of the relative reactivities of the compounds. A mix of 50 percent weight of silica (diatomaceous earth MN-53) with CaO (e.g., 100 g of MN-53 and 100 g of $Ca(OH)_2$) appears to give the optimum performance. These amounts translate into 1.78 mol of $Ca(OH)_2$ and 1.40 mol of SiO_2, assuming that MN-53 is about 84 weight percent SiO_2 (see Table 5-2). This mole ratio is nearly 1:1, which happens to agree with the hypothetical reaction illustrated in Figure 5-14 (Smith, 1986). Previous reports indicate that the formation of calcium silicate hydrates is most common in the range of 40 to 53 weight percent of silica in the mixture of calcium/silica (Taylor, 1964).

The results of differential scanning calorimetry tests are presented in Figure 5-15. Testing was performed for the whole range of silica concentration (weight percent), as well as for pure MN-53 and

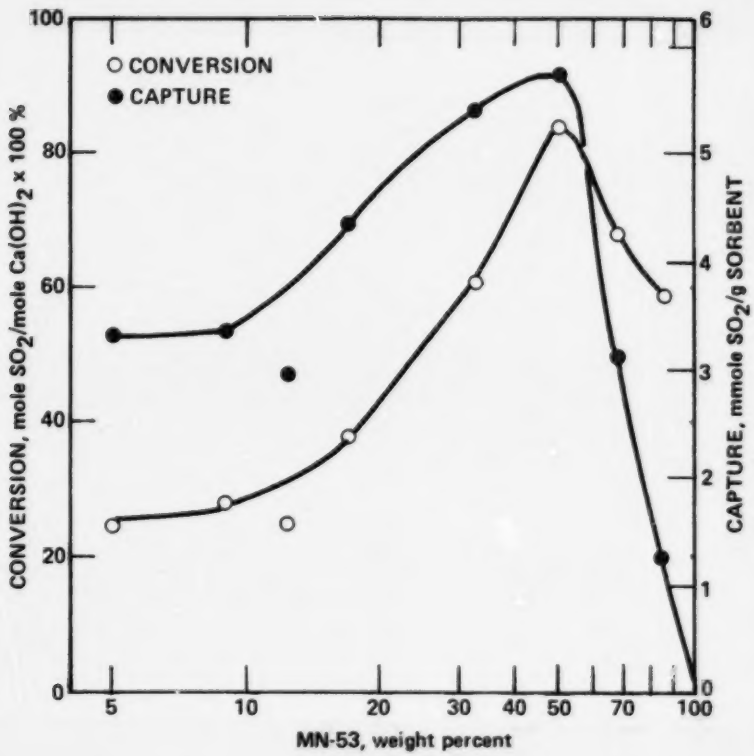


Figure 5-13. The effect of silica weight percent on sample reactivity (conditions in the sand-bed reactor the same as in Figure 5-1).

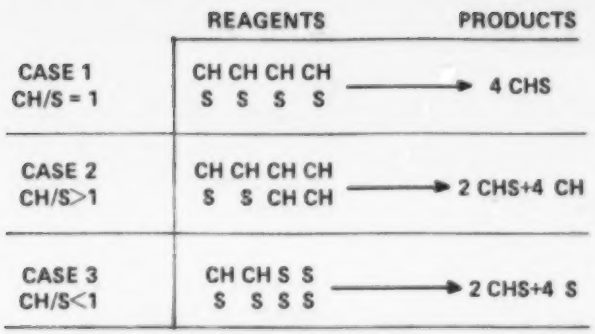


Figure 5-14. Hypothetical reaction between $Ca(OH)_2$ and diatomaceous earth (Smith, 1986); CH = $Ca(OH)_2$, S = SO_2, CHS = $CaO \cdot SiO_2 \cdot H_2O$.

$Ca(OH)_2$. There is an evidence of new products being formed. New peaks can be seen for samples hydrated at 90 °C (194 °F) for 4 h. The first peak occurs at about 145 °C (293 °F), and a small exothermal peak can be seen at about 330 °C (626 °F) for samples at the weight ratios of diatomaceous earth CaO of 1:2, 1:5, and 1:7. For the samples with the weight ratios of 1:1 and 1:2, an additional peak can be seen at 450 °C (842 °F). These peaks seem to be well within the range reported by Glasser (1970) as characteristic for tobermorites. The peak at 480 °C in Figure 5-15 and characteristic for $Ca(OH)_2$ is drawn out of proportion. It was really 5 times higher than the peak at 145 °C (293 °F) for the ratio of 1:1, 10 times higher than the peak at 145 °C (293 °F) for the ratio of 1:2, and 25 times higher than the peak at 145 °C (293 °F) for the ratios of 1:5 and 1:7.

The B.E.T. surface areas measured for the samples of diatomaceous earth/CaO are provided in Table 5-6. The reactivity of the samples increased with increasing surface area for diatomaceous earth/CaO ratios in the range from 1:19 to 1:1. Table 5-6 also presents the results of x-ray powder diffraction analysis. They seem to confirm the results from the differential scanning calorimetry measurements, indicating that sorbent reactivity decreased with the increasing amount of uncombined $Ca(OH)_2$ (less calcium silicates produced).

The effect of relative humidity in the packed bed reactor on the reactivity of samples was tested for the MN-53 and Kenite natural diatomaceous earths. Both samples were prepared at the silica/CaO ratio of 1:1 and hydrated at 90 °C (194 °F) for 4 h. The temperature of the packed bed reactor was held constant at 64.4 °C (148 °F), SO_2 concentration was 1,000 ppm, and relative humidity was varied from 30 to 80 percent. As can be seen in Figure 5-16, the conversion of $Ca(OH)_2$ and the SO_2 capture did not increase for relative humidities above 60 percent.

Two experiments were performed with MN-53/CaO sorbent at the ratio of 1, exposed to 1,000 ppm SO_2 at a relative humidity of 60 percent and for various packed bed reactor temperatures. At 74.4 and 84.4 °C (166 and 184 °F), the $Ca(OH)_2$ conversion was 62 and 61 percent, respectively (4.16 and 4.14 mmol SO_2/g of sorbent, respectively).

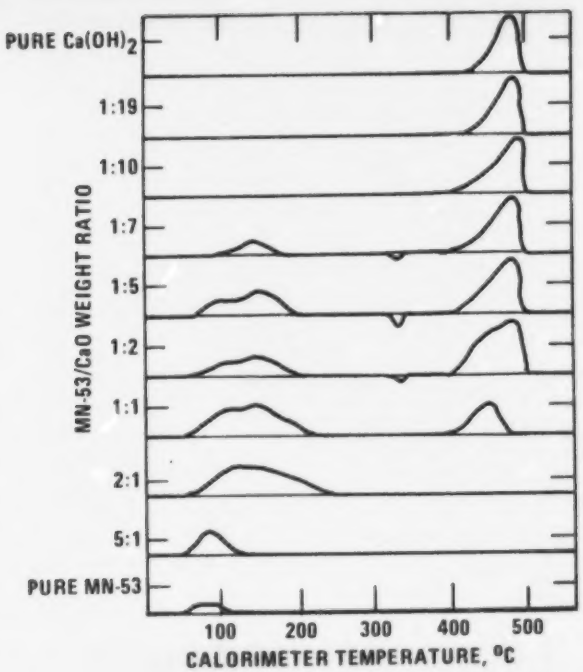


Figure 5-15. Results of differential scanning calorimetry tests [all samples prepared by 4 h hydration at 90 °C (194 °F)].

Table 5-6. Characterization of MN-53/CaO Sorbents

Promoter Weight Percent	Available $Ca(OH)_2$ Weight Percent	B.E.T.[a] Surface Area (m^2/g)	Intensity[b] $Ca(OH)_2$	Intensity[b] $CaCO_3$[c]	Conversion[d] (%)	SO_2 Capture (mmol/g)
5	90	41	100	7	24	3.16
9	76	33	83	14	28	3.40
13	62	52	53	10	22	2.60
17	70	56	52	8	38	4.32
33	48	59	40	12	61	5.47
50	none	90	18	20	84	5.68
67	4	115	0	42	68	3.07
83	3	72	0	24	59	1.34

[a] MN-53 has a surface area of 56 m^2/g.
[b] Intensity of peaks on x-ray powder diffractogram.
[c] Based on a single peak at 2 = 29.45° (3.03) - Low reliability.
[d] After 1 h in the sand bed reactor operated at 60 percent relative humidity, 64.4 °C (148 °F) temperature, and 1,000 ppm SO_2 concentration.

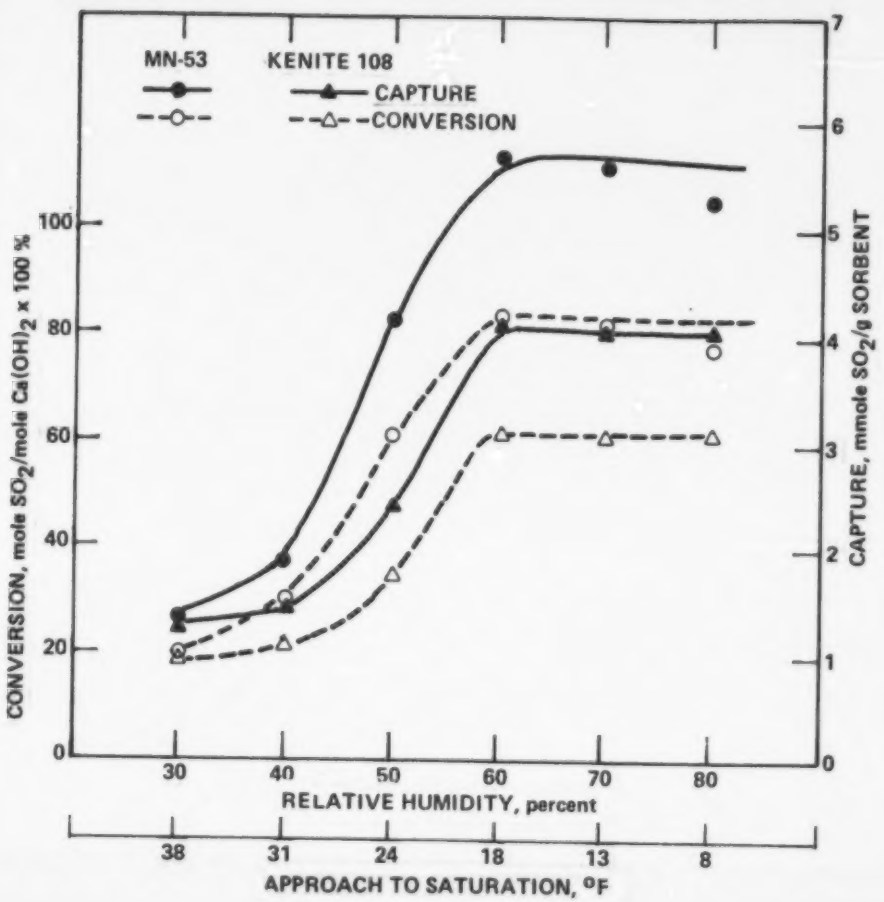


Figure 5-16. The effect of relative humidity on sample reactivity.

At the lower SO_2 concentration of 500 ppm instead of 1,000 ppm, with other conditions the same, the conversions of MN-53 and Kenite-based sorbents were 72 and 61 percent, respectively (4.96 and 4.05 mmol SO_2/g of sorbent, respectively).

The morphology of the prepared samples was characterized using SEM analysis. The sample of MN-53/CaO at the ratio of 1:10 is illustrated in Figure 5-17. Separate chunks of $Ca(OH)_2$ and of diatomaceous earth can be seen in this figure. Figure 5-18 shows the sample hydrated at the ratio of MN-53/CaO of 1:15. Finally, Figures 5-19 through 5-22 detail the MN-53/CaO sample at the ratio of 1:1. The surface area, as shown by different degrees of magnification in these pictures, is clearly well developed.

5.5 COST OF ALTERNATE SILICEOUS MATERIALS

Among the key issues which need to be resolved are the cost and availability of the alternate siliceous materials. Table 5-7 provides unit costs and locations for the best identified siliceous materials. The most attractive, MN-53 from Eagle-Picher, is mined in Clark, Nevada, but transportation costs would add significantly to the operational costs if the east coast was the location of the commercial application. This technology could be fully competitive with other retrofit options if known deposits of diatomaceous earth in the eastern U.S. (e.g., Florida, Maine, Maryland, and Virginia) would be brought into commercial operation.

Aside from delivery charges, preparation costs need to be optimized. A significant amount of energy would be required to dry the sorbent after it was hydrated. One option would be to paste handling equipment to mix prepared slurry with dry recycled solids and to introduce the moist product into the duct. Another option would be to use pressure hydration to produce powdered reagent.

5.6 CONCLUSIONS

From this study, the following conclusions may be drawn:

1. Siliceous materials from sources other than flyash are also effective in enhancing the reactivity of lime with SO_2 by slurrying lime and silica at elevated temperatures.
2. Among the siliceous materials tested, natural grade diatomaceous earth and bentonitic clay were found to be the most effective in producing reactive sorbent by slurrying with lime.

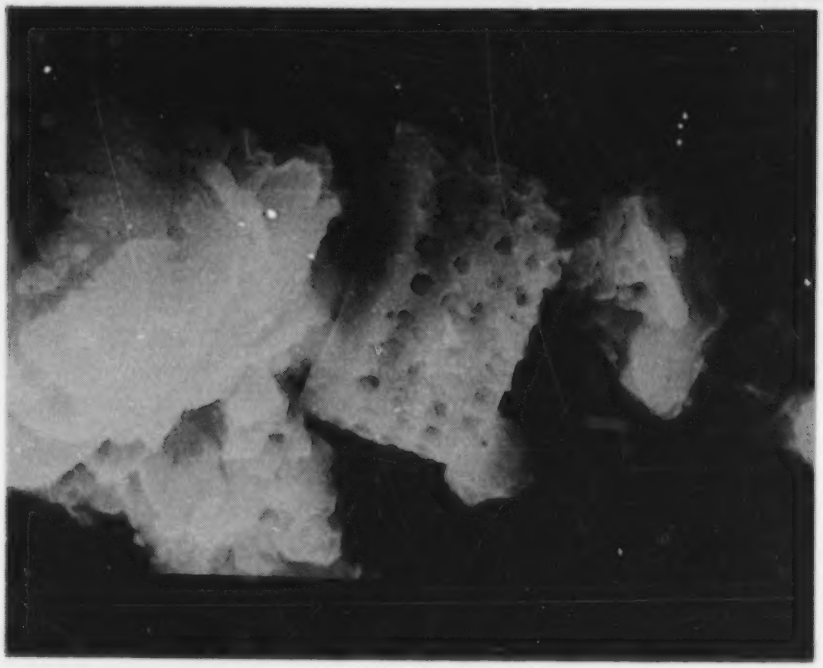


Figure 5-17. SEM photograph of MN-53/CaO sample (ratio 1:10, 5,000x).

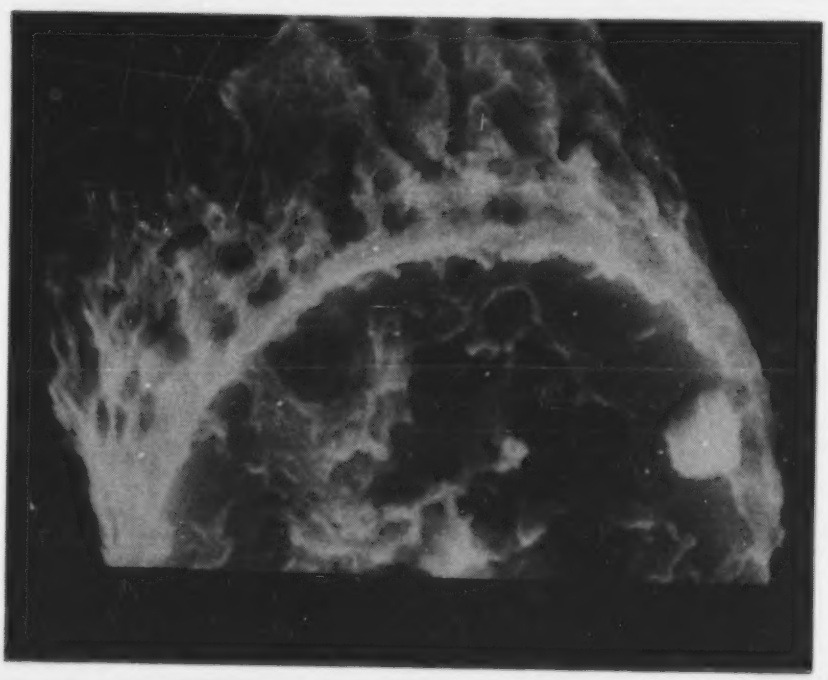


Figure 5-18. SEM photograph of MN-53/CaO sample (ratio 1:5, 10,000).

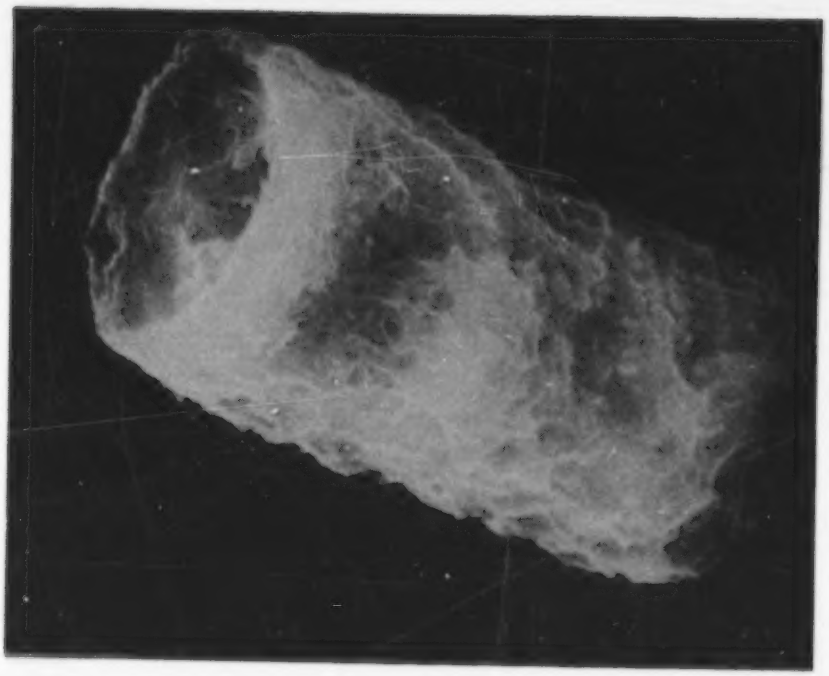


Figure 5-19. SEM photograph of MN-53/CaO sample (ratio 1:1, 5,000x).

Figure 5-20. SEM photograph of MN-53/CaO sample (ratio 1:1, 5,000x).

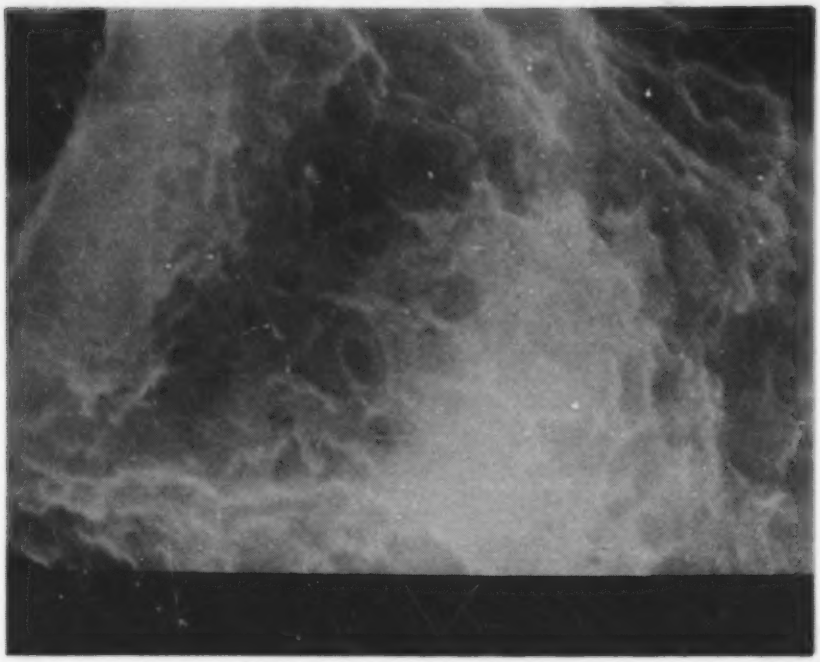


Figure 5-21. SEM photograph of MN-53/CaO sample (ratio 1:1, 10,000x).

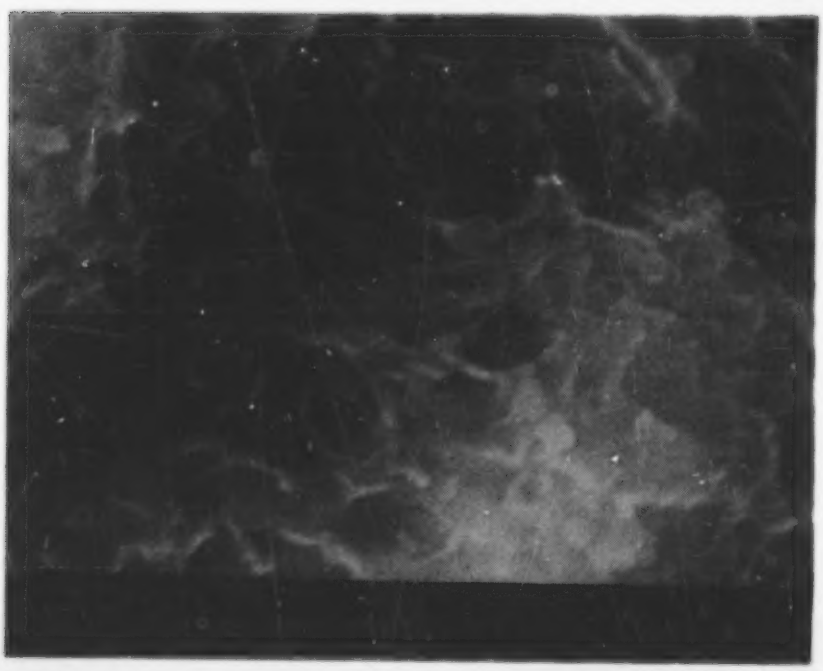


Figure 5-22. SEM photograph of MN-53/CaO sample (ratio 1:1, 20,000x).

Table 5-7. Availability of Promoters

Trade Name	Manufacturer	Material Type	Location of Deposit	Price $/ton	Minimum[a] Quantity tons
Filtrol 105	Harshaw-Filtrol	Acid Activated Montmorillonitic Clay	Jackson, Mississippi	267 78	20 22
Volclay 325	American Colloid Company	Raw Na-Montmorillonite	Bell Fourche, South Dakota	78	22
Bentonite 149	Whittaker, Clard & Daniels, Inc.	Montmorillonitic Clay	Bell Fourche, South Dakota	83	18
MN-53	Eagle-Picher Industries, Inc.	Natural Diatomaceous Earth	Clark, Nevada	100	22
Kenite 108	Witco Chemical Corporation	Natural Diatomaceous Earth	Quincy, Washington	168	21

a Minimum amount to obtain price from proceeding column.

3. The reactivity of the sorbents prepared by slurrying cryptocrystalline silica with lime can be correlated with B.E.T. surface area, i.e., the reactivity increased with increasing surface area of the prepared sorbents.
4. The most reactive sorbent was produced by slurrying siliceous material with lime at a silica/CaO ratio of about 1 to 1.
5. Calcium silicate hydrates were formed during the slurrying process. The high reactivity of the produced product can be partially attributed to the large surface area of the calcium silicate as well as its great water retaining capability.

SECTION 6

EFFECTS OF ADDITIVES ON SORBENT REACTIVITY

The objectives of this area of research were to evaluate the effectiveness of additives in enhancing the reactivity of sorbents produced by flyash/lime slurrying. The additives tested included sodium hydroxide, sodium phosphate, ammonium phosphate, and phosphoric acid.

6.1 SODIUM HYDROXIDE

A test series was performed in which NaOH was added to the slurry of flyash and lime (using a flyash/CaO weight ratio of 3). Figure 6-1 indicates the effect of NaOH addition during sorbent preparation on the conversion of sorbent with SO_2, as measured in the packed bed reactor at normal test conditions. In these experiments the absolute amount of NaOH added to the flyash/lime slurry was a constant 0.1 mol NaOH/mol $Ca(OH)_2$. The concentration of NaOH was varied from 0.05 to 0.25 N by changing the amount of water added, therefore changing the percentage of solids in the slurry. The mixtures were slurried for 4 or 8 h at 65 or 90 °C (149 or 194 °F). The effect of the NaOH solution concentration varied with time and temperature of slurrying. No enhancement by NaOH was seen at the lower slurrying temperature [65 °C (149 °F)] using a short residence time in the slurrying tank (4 h). The most significant enhancement was seen when 0.25 N NaOH was added to the sample slurried for 8 h at 90 °C (194 °F) where the conversion in the packed bed reactor was 0.5 mol SO_2/mol $Ca(OH)_2$, compared with 0.35 mol SO_2/mol $Ca(OH)_2$ without NaOH addition. These test results seem to support the hypothesis that the dissolution of silica in the flyash is the limiting step for the reaction between flyash and lime during slurrying.

Further sodium hydroxide testing was performed, using the NaOH/$Ca(OH)_2$ ratio as a variable test parameter. The flyash/$Ca(OH)_2$ sorbent was prepared at the weight ratio of 2.3:1 and slurried at 90 °C (194 °F) for 8 h. Two levels of NaOH concentration, 0.1 and 0.25 N, were maintained during this

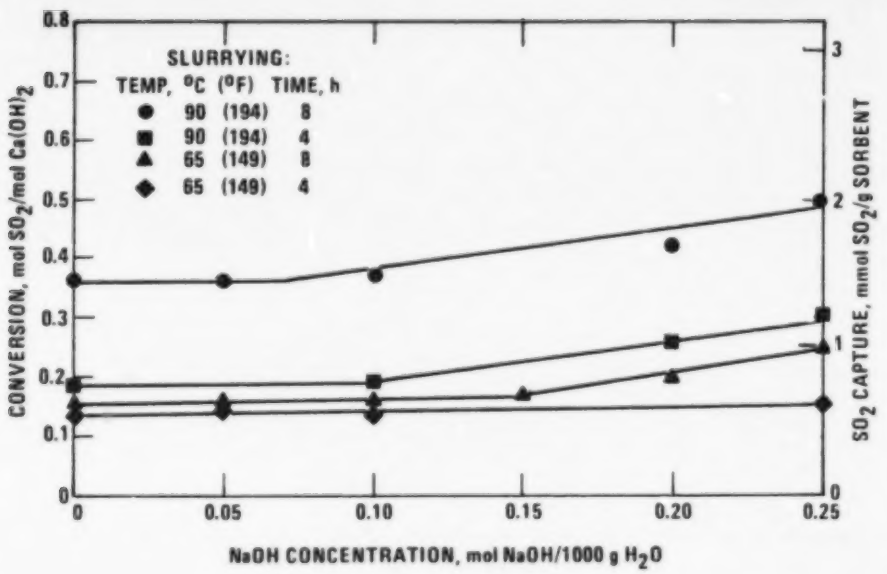


Figure 6-1. The effect of slurrying conditions on the enhancement of reactivity of flyash/$Ca(OH)_2$ samples by NaOH (flyash/CaO weight ratio = 3:1).

study. The results are presented in Figure 6-2. In this study a maximum in sorbent conversion occurred at about 4 mol percent of NaOH additive [$Ca(OH)_2$ based]. After exposure to 500 ppm SO_2 in the packed bed reactor, the conversion reached 0.55 mol SO_2/mol $Ca(OH)_2$ when the concentration of NaOH was 0.25 N. Lowering the concentration of NaOH to 0.1 N, by increasing the amount of water added to the sample, decreased the conversion to 0.45 mol SO_2/mol $Ca(OH)_2$.

Finally, parametric tests were run to investigate the effect of relative humidity on the reactivity of flyash/$Ca(OH)_2$ sorbent prepared at the weight ratio of 2.3:1, with and without additive. Two sorbents were compared: one was slurried at 90 °C (194 °F) for 24 h, while the second was slurried at 90 °C (194 °F) for only 8 h but with 4 mol percent of NaOH additive. The results are presented in Figure 6-3, along with those for a reagent grade $Ca(OH)_2$ for comparison. The reactivity of the sorbent prepared with NaOH additive is clearly higher at high humidities than the reactivity of sorbent slurried at 90 °C (194 °F) for 24 h without the additive. The final conversions were 0.54 and 0.51 mol SO_2/mol $Ca(OH)_2$, respectively, when flyash/$Ca(OH)_2$ sorbents prepared with and without NaOH were exposed to 500 ppm SO_2 in the packed bed reactor operating at 60 percent relative humidity (Δt_s = 10 °C). At 80 percent relative humidity in the reactor (Δt_s = 4 °C), the corresponding conversions were 0.76 and 0.67 mol SO_2/mol $Ca(OH)_2$. The increased difference in the reactivity of these two sorbents with increased relative humidity would be expected, due to the deliquescent properties of NaOH. When the relative humidity is higher than about 50 percent the NaOH also absorbs water, in addition to the sorbent itself, while at lower relative humidity the sorbent alone absorbs water. Thus, at higher relative humidity the reactivity of the sorbent with a deliquescent additive is increased.

Assuming that the flyash used was about 50 percent silica, the data in Figure 6-2 appear to be consistent with data on the production of α-dicalcium silicate hydrate (Sercale, 1980). Leineweber (1964) reported 6.7 mol percent NaOH as the optimum amount for the formation of α-dicalcium silicate hydrate when CaO was hydrated with diatomaceous earth at a weight ratio of 1.9:1. α-dicalcium silicate hydrate is probably the most reactive silicate with SO_2.

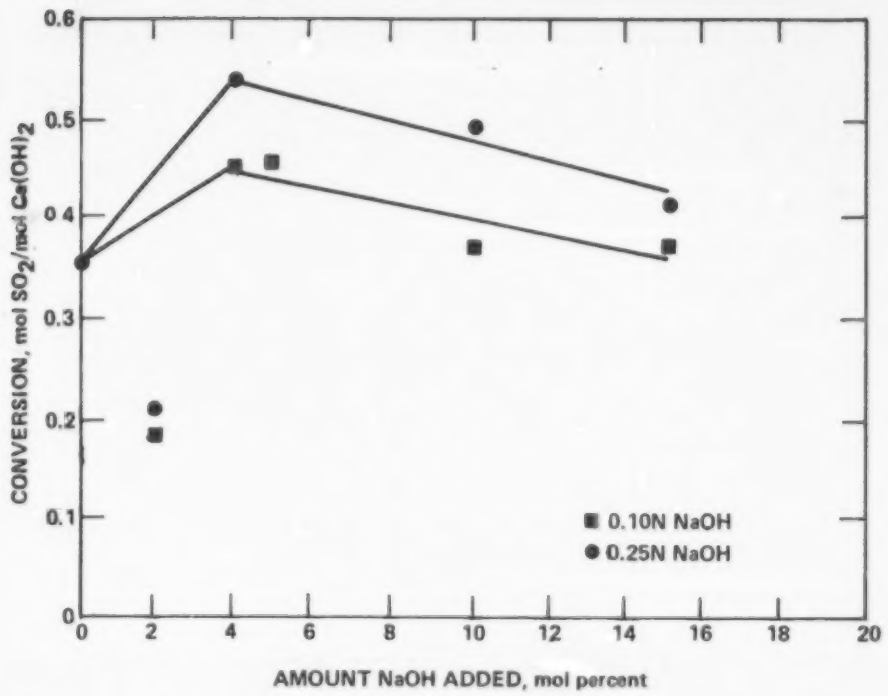


Figure 6-2. The effect of NaOH addition during slurrying on the reactivity of dry sorbent in the sand-bed reactor [preparation conditions: slurrying at 90 °C (194 °F) for 8 h; sand-bed reactor conditions: 60 percent relative humidity, 64.4 °C (148 °F) temperature, and 500 ppm SO_2 concentration].

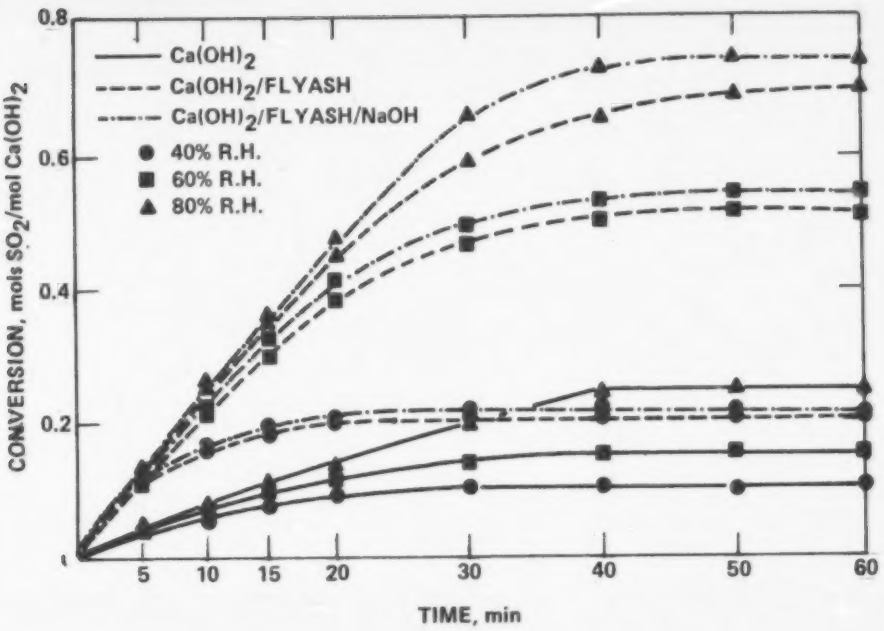


Figure 6-3. Combined deliquescent and flyash-digesting effect of NaOH (slurrying: 8 h at 90 °C; sand-bed conditions: 500 ppm SO_2, 64 °C, relative humidity as shown above).

6.2 PHOSPHATES

Three phosphate additives were tested for enhancing the reactivity of the sorbent prepared at a weight ratio of flyash-to-$Ca(OH)_2$ of 2.3:1. The additives tested were $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and H_3PO_4. In Figure 6-4 the results of tests employing sodium and ammonium phosphates and phosphoric acid give the conversion as a function of the absolute amount of phosphate added for both $Ca(OH)_2$ and CaO [5 g of flyash with 2.2 g of $Ca(OH)_2$ or 5 g of flyash with 1.67 g CaO; i.e., the flyash-to-CaO weight ratio was 3:1 in both cases]. All data in Figure 6-4 were obtained for sorbent prepared for slurrying flyash with lime at 90 °C (194 °F) for 8 h and, after drying, exposing the dry sorbent to 500 ppm SO_2 in the packed bed reactor operated at 64 °C (147 °F) and 60 percent relative humidity [Δt_s = 10 °C (18 °F)]. The maximum conversions obtained with flyash/$Ca(OH)_2$ sorbents were achieved when 4 mol percent of either sodium or ammonium phosphate was added. With H_3PO_4 as the additive, the maximum conversion was when 5 mol percent was added. These results suggest that the enhanced conversion of $Ca(OH)_2$ was probably due to the increased dissolution of flyash resulting from the presence of PO_4-ion and, consequently, the increased formation of calcium silicate hydrates. When CaO instead of $Ca(OH)_2$ was slurried with flyash the amount of phosphate needed to reach the same degree of reactivity was 50 and 70 percent, respectively, when $(NH_4)_2HPO_4$ and $Na_2HPO_4 \cdot 7H_2O$ were used. For example, a maximum conversion of 0.5 mol SO_2/mol $Ca(OH)_2$ was reached when 4 and 8 mol percent of $(NH_4)HPO_4$ were added during the slurrying of flyash with CaO and $Ca(OH)_2$. This result may stem from the dispersing properties of phosphates, present during the hydration of CaO, which create finer particles in the product compared to those obtained using $Ca(OH)_2$. These smaller particles would react more easily with silica from the flyash, than would the coarser $Ca(OH)_2$ particles, to form calcium silicate.

6.3 CONCLUSIONS

1. The reactivity of sorbents, with respect to dry SO_2 removal prepared by using a weight ratio of flyash to lime of 2.3 to 1, increased with the application of additives such as NaOH, $Na_2HPO_4 \cdot 7H_2O$, $(NH_4)_2HPO_4$, and H_3PO_3 during the slurrying process.

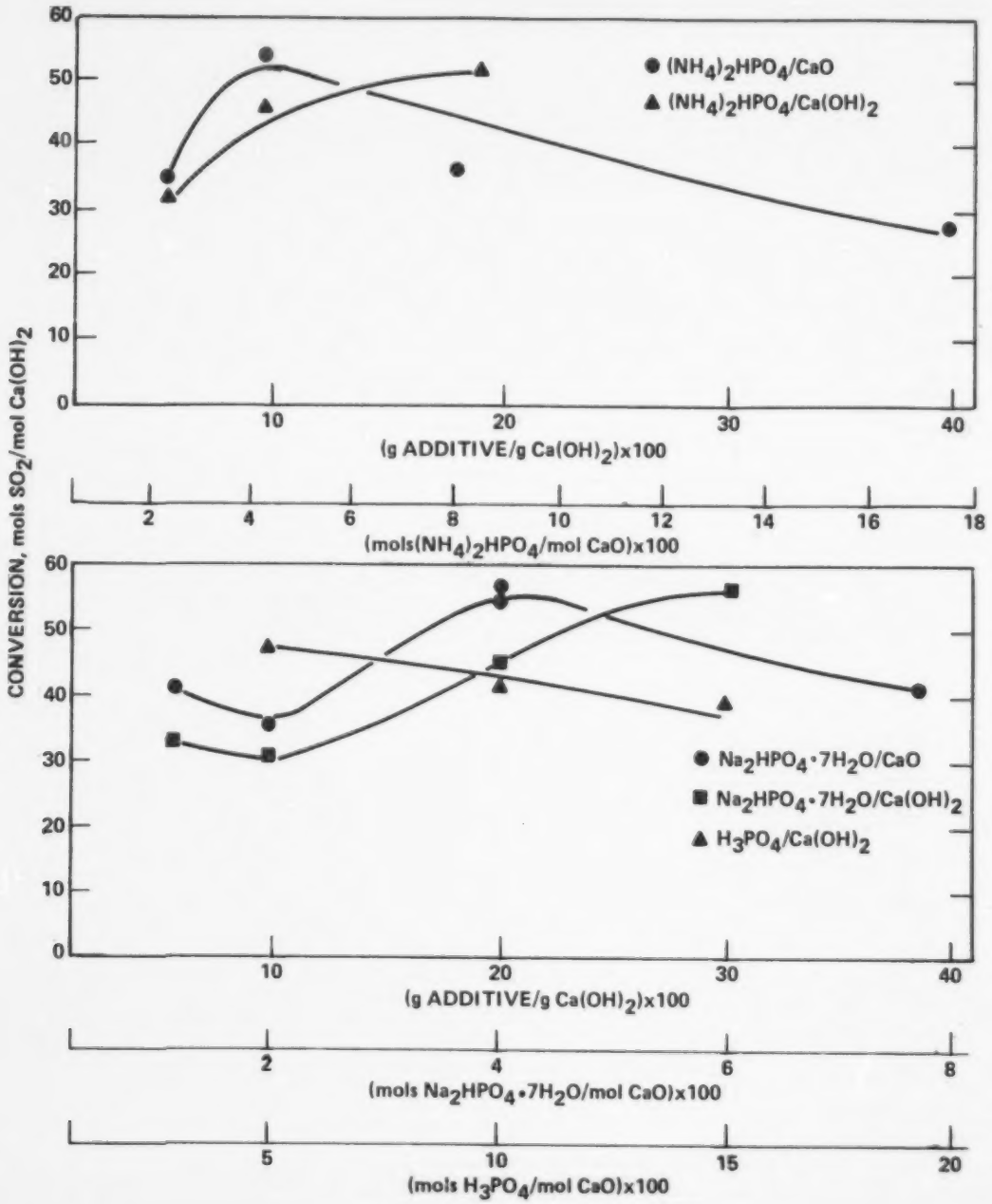


Figure 6-4. Reactivity enhancement of flyash/$Ca(OH)_2$ and flyash/CaO sorbents by use of additives (slurrying and sand-bed conditions the same as in Figure 6-3).

2. The maximum sorbent reactivity enhancement was obtained by using 4 to 8 mol percent additives relative to the amount of $Ca(OH)_2$.
3. Sodium hydroxide was the most effective additive in enhancing the reactivity of the hydrates at high humidity, probably due to its deliquescent properties.
4. Phosphates were more effective additives when used with CaO rather than with $Ca(OH)_2$, probably due to the dispersing properties of phosphates which could result in finer particles during CaO slaking.

SECTION 7

PRESSURE HYDRATION EVALUATION

This section describes bench-scale experimental work aimed at producing pressure hydrated calcium silicate for dry SO_2 control. It focuses on the pressure hydration of flyash or diatomaceous earth with $Ca(OH)_2$, with the primary goal of reducing the time required for hydration and lowering the weight ratio of siliceous materials to lime.

7.1 PRESSURE HYDRATION OF FLYASH/HYDRATED LIME MIXTURES

The conversion of $Ca(OH)_2$ increased with increased weight ratios of flyash to $Ca(OH)_2$ when atmospheric hydration was used. No significant increase of the conversion could be seen when samples at a weight ratio ranging from 1:1 to 5:1 were hydrated atmospherically at 90 °C (194 °F) for 4 h. During this work, pressure-hydrated sorbents with flyash-to-$Ca(OH)_2$ weight ratios ranging from 1:2 to 5:1 were investigated. The silica source was flyash from the Clinch River Power Plant, obtained from burning eastern bituminous coal which contains about 50 percent SiO_2. Figure 7-1 presents the reactivity of the sorbent as a function of flyash-to-$Ca(OH)_2$ weight ratio. All samples tested were prepared by pressure hydration at 150 °C (476 kPa) [302 °F (69 psi)] for 2 h at a water-to-solids ratio of 15:1 (6 percent solids in the slurry). The samples were then dewatered and dried. The resulting dry powdered sorbent was mixed with sand and exposed to 500 ppm SO_2 in the packed reactor, operated at 64 °C (147 °F) and 60 percent relative humidity [Δt_s = 10 °C (18 °F)]. As can be seen in Figure 7-1, conversion of $Ca(OH)_2$ in the sorbent increased with increasing flyash-to-$Ca(OH)_2$ weight ratios. The measured B.E.T. surface area for pressure-hydrated samples (see in Figure 7-1) generally increased with increasing weight ratios of flyash to lime. When a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1 was used, the conversion was 0.19 and 0.42 mol SO_2/mol $Ca(OH)_2$, respectively, when atmospheric and pressure hydration at the conditions described above were used. Based on these results, flyash/$Ca(OH)_2$ mixtures prepared by pressure hydration at

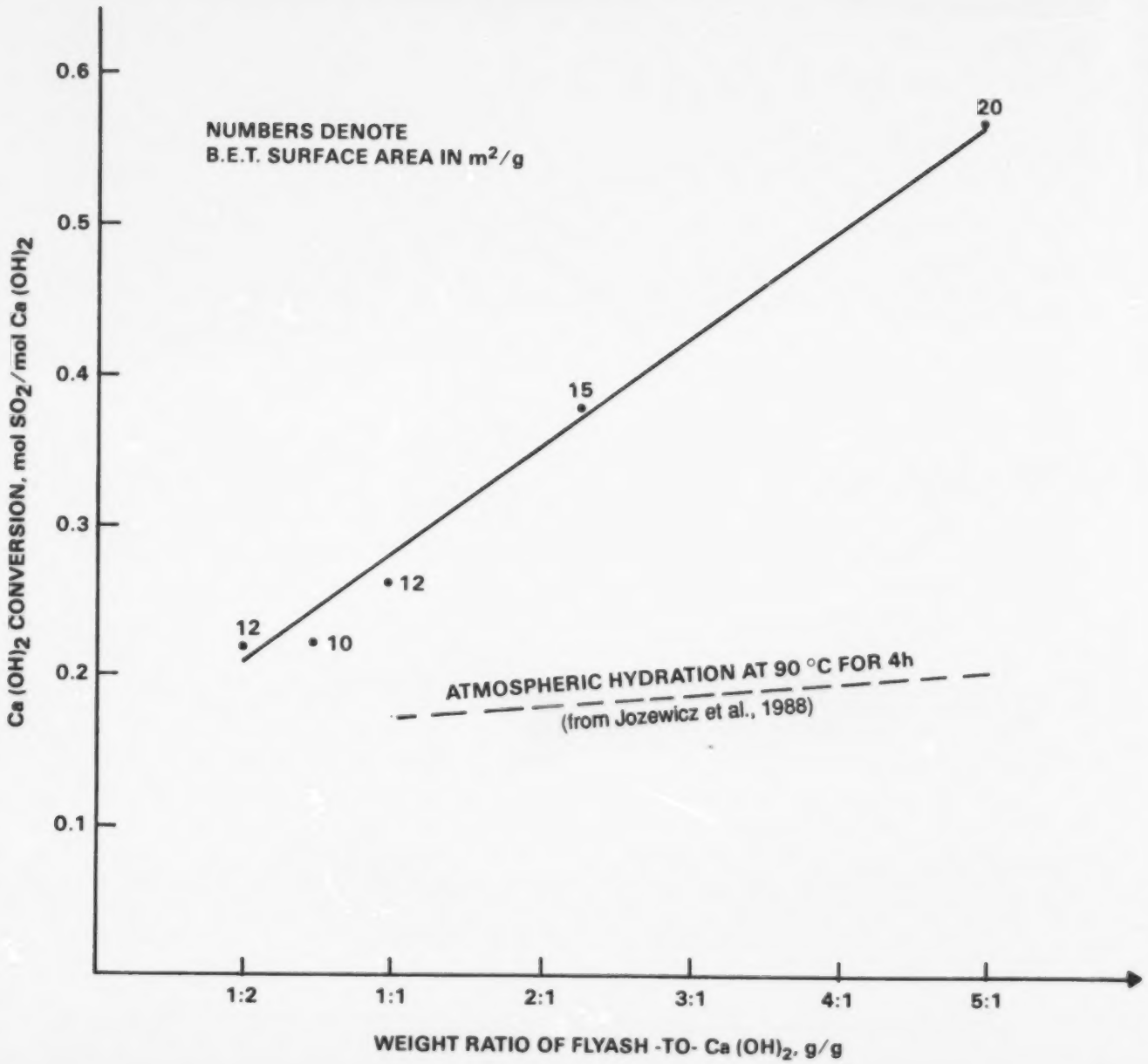


Figure 7-1. The effect of weight ratio of flyash to $Ca(OH)_2$ on the reactivity of pressure-hydrated sorbents [sand-bed reactor conditions: relative humidity 60 percent, temperature 64 °C (147 °F), SO_2 concentration 500 ppm; pressure hydrator conditions: temperature 150 °C (302 °F), 2 h].

weight ratios of 1:1 and 2.3:1 were recommended for pilot plant testing in AEERL's 100 m^3/h (58 cfm) spray dryer/baghouse or humidification/dry-injection/baghouse system.

Also investigated was the effect of the time of pressure hydration of flyash and $Ca(OH)_2$, at the weight ratio of 2.3:1, on the conversion of $Ca(OH)_2$ in the packed bed reactor. The results are presented in Figure 7-2. The conversion for the pressure-hydrated mixture at 150 °C (476 kPa) [302 °F (69 psi)] followed the trend observed earlier for atmospheric-hydrated mixtures. This trend indicated that, for a constant weight ratio of flyash to $Ca(OH)_2$ and a constant temperature of hydration, the conversion of $Ca(OH)_2$ increased with increased time of hydration. For pressure hydration at 180 °C (1,000 kPa) [356 °F (145 psi)] and 230 °C (2,793 kPa) [446 °F (405 psi)] and with reactants at the same weight ratio, a maximum $Ca(OH)_2$ conversion occurred after 4 and 1 h, respectively. This phenomenon was probably due to the fact that all of the silica available (active silica) for the reaction with lime was used, and more rapidly at 230 °C (446 °F) than at 180 °C (356 °F). Similar behavior was observed when flyash and $Ca(OH)_2$ at a weight ratio of 1:1 were pressure hydrated at 120 and 150 °C (248 and 302 °F). These results are presented in Figure 7-3. Maximum conversions of $Ca(OH)_2$ of 0.38 mol SO_2/mol $Ca(OH)_2$ after 1 h, and 0.45 mol SO_2/mol $Ca(OH)_2$ after 2 h, were observed for sorbents pressure hydrated at 150 and 120 °C (302 and 248 °F), respectively. No enhancement of conversion above the baseline of 0.17 mol SO_2/mol $Ca(OH)_2$ occurred when the mixture of flyash and $Ca(OH)_2$ at a weight ratio of 1:1 was hydrated atmospherically for a period ranging from 1 to 5 h.

Comparison of atmospheric hydration reactivity data with results obtained for sorbents which were pressure hydrated (Figures 7-2 and 7-3) clearly shows that a significant decrease of the time of hydration is possible when pressure, rather than atmospheric, hydration is used. Atmospheric hydration at 90 °C (194 °F) for 8 h was required to enhance the conversion of $Ca(OH)_2$ up to 0.35 mol SO_2/mol $Ca(OH)_2$, when the weight ratio of flyash to $Ca(OH)_2$ was 2.3:1. The same conversion was achieved for the same reactants and weight ratio after pressure hydration at 150 °C (69 psi) [302 °F (476 kPa)] for 1 h. The effect of pressure hydration on the conversion of $Ca(OH)_2$ is even more dramatic when the flyash-to-$Ca(OH)_2$ weight ratio is 1:1 instead of 2.3:1. A conversion as high as 0.45 mol SO_2/mol

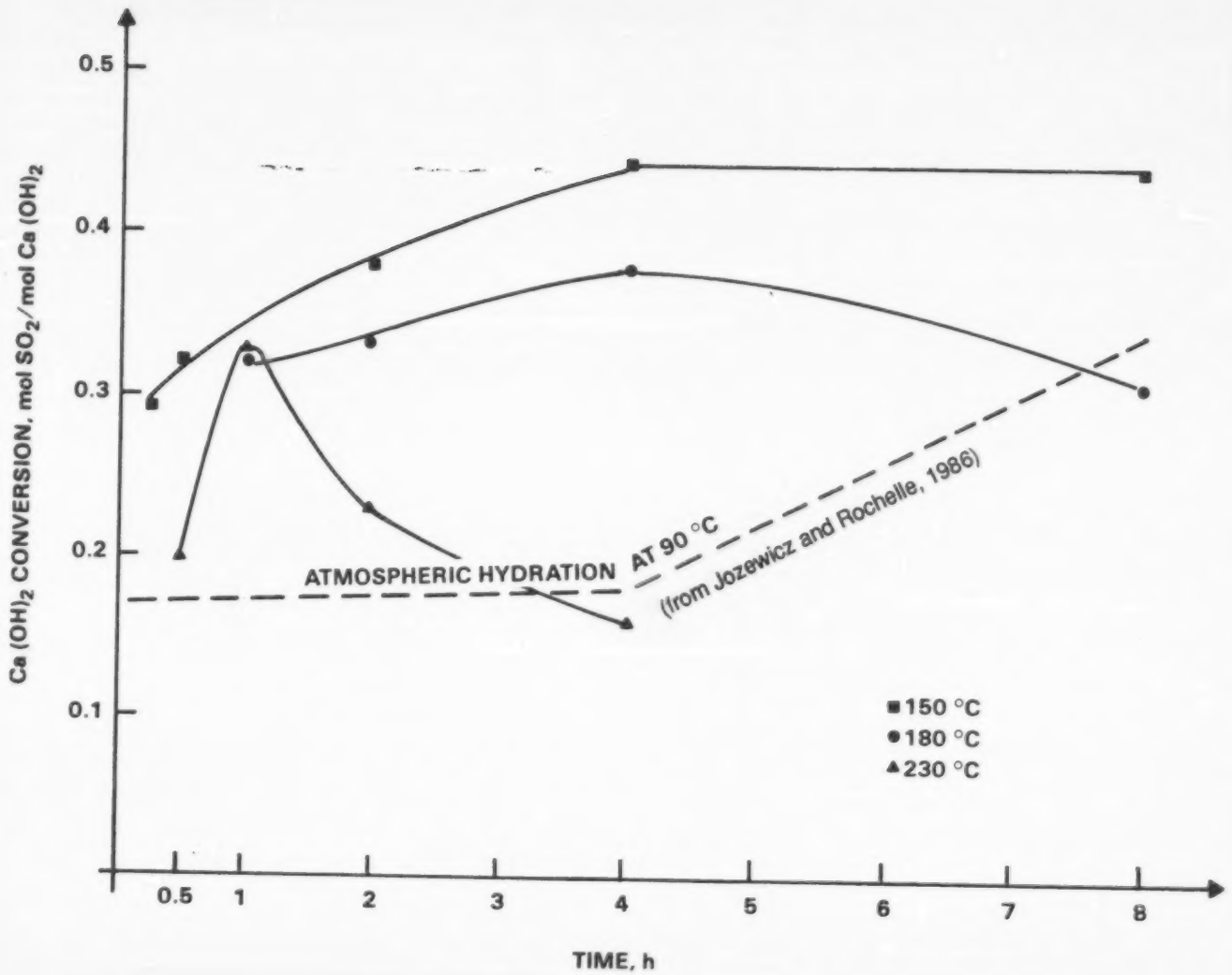


Figure 7-2. Combined time and temperature effects of pressure hydration on the reactivity of sorbent prepared at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 (sand-bed reactor conditions the same as in Figure 7-1).

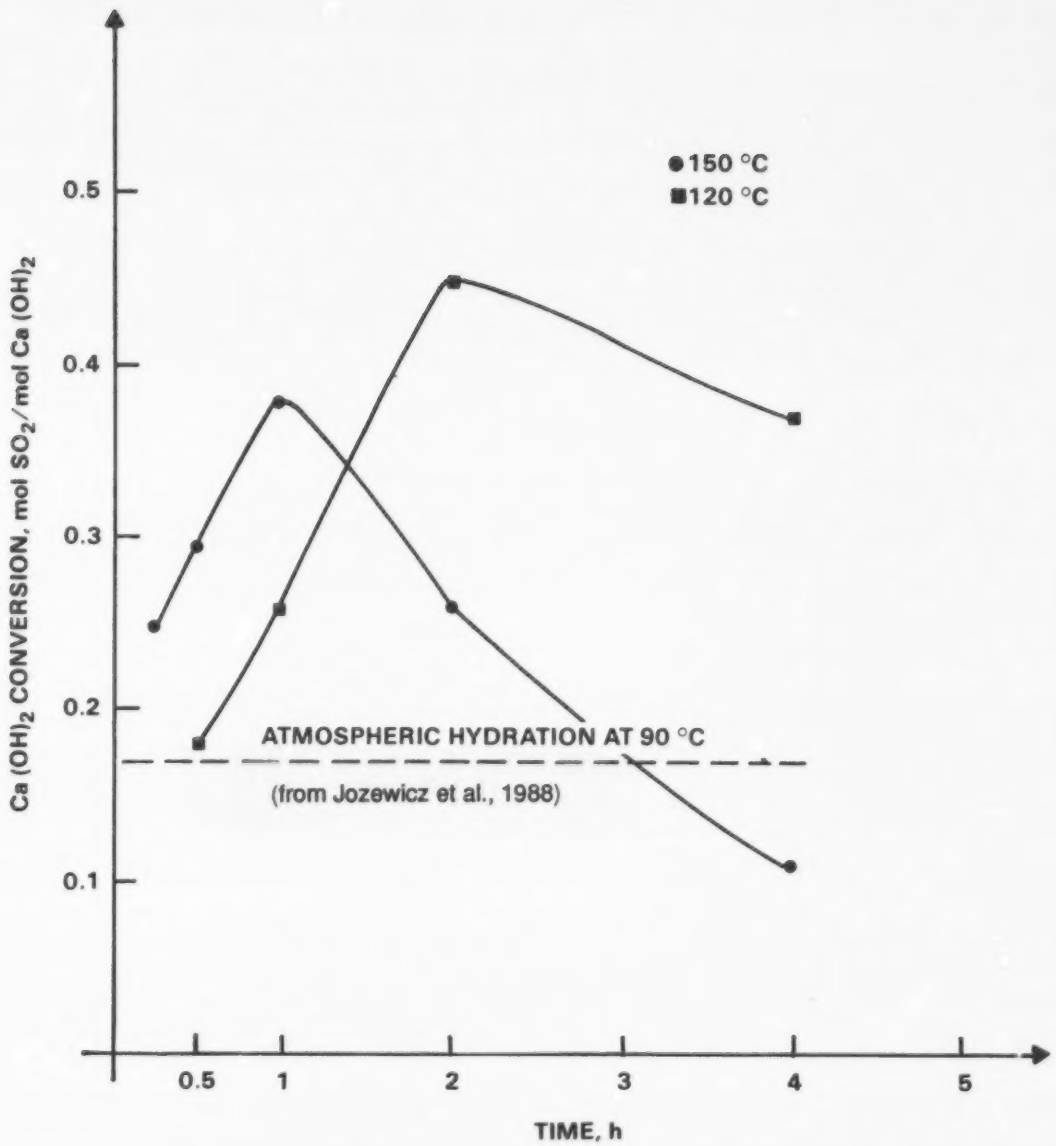


Figure 7-3. Combined time and temperature effects of pressure hydration on the reactivity of sorbent prepared at the weight ratio of flyash to $Ca(OH)_2$ of 1:1 (sand-bed reactor conditions the same as in Figure 7-1).

$Ca(OH)_2$ was observed after 2 h of pressure hydration at 120 °C (200 kPa) [248 °F (29 psi)]. Even after a short hydration time of 15 min at 120 °C (248 °F), it was possible to achieve a $Ca(OH)_2$ conversion of 0.25 mol SO_2/mol $Ca(OH)_2$.

To investigate the effect of hydration temperature on the reactivity of $Ca(OH)_2$, experiments were performed on sorbents prepared with flyash-to-$Ca(OH)_2$ weight ratios of 2.3:1 and 1:1 by pressure hydration for 4 h at temperatures ranging from 100 °C (101 kPa) [212 °F (14.7 psi)] to 230 °C (2,793 kPa) [446 °F (405 psi)]. The packed bed reactor results are shown as solid lines in Figure 7-4. When a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 was used, the conversion was a maximum of 0.46 mol SO_2/mol $Ca(OH)_2$ for sorbent pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)]. A further increase of the hydration temperature resulted in a gradually decreasing conversion, reaching the baseline value of 0.17 mol SO_2/mol $Ca(OH)_2$ at 230 °C (2,793 kPa) [446 °F (405 psi)]. The decreasing conversion of $Ca(OH)_2$ with temperatures in the range from 150 to 230 °C (302 to 446 °F), compared with the range from 100 to 150 °C (212 to 302 °F), is probably caused by the formation of another phase. Taylor (1964) reported that calcium silicates with significantly less molecular water may be formed in the 150 to 230 °C (302 to 446 °F) temperature range. However, the results (see the solid lines in Figure 7-4) are somewhat biased in that the observed maximum conversion at a given temperature might have been different from values presented for the 4 h pressure hydrations. For example, when using a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, the maximum conversion of $Ca(OH)_2$ at 230 °C (2,793 kPa) [446 °F (405 psi)] was 0.33 mol SO_2/mol $Ca(OH)_2$ for sorbent hydrated for 1 h. The conversion of sorbent prepared at the same weight ratio of flyash to $Ca(OH)_2$, but pressure hydrated at 230 °C (446 °F) for 4 h (value shown in Figure 7-4), was much lower [0.18 mol SO_2/mol $Ca(OH)_2$] for the reasons discussed earlier. When considering the effect of temperature, the maximum values of conversion at a given temperature must be considered to compensate for the time/temperature dependence of conversion. The maximum values for the range of 180 to 230 °C (356 to 446 °F) are presented as broken lines in Figure 7-4. The values for the 150 to 180 °C (302 to 356 °F) range are identical with those for the 4 h pressure hydrations. As can be seen, the maximum values of conversion somewhat offset the effect of increasing temperature. The optimum

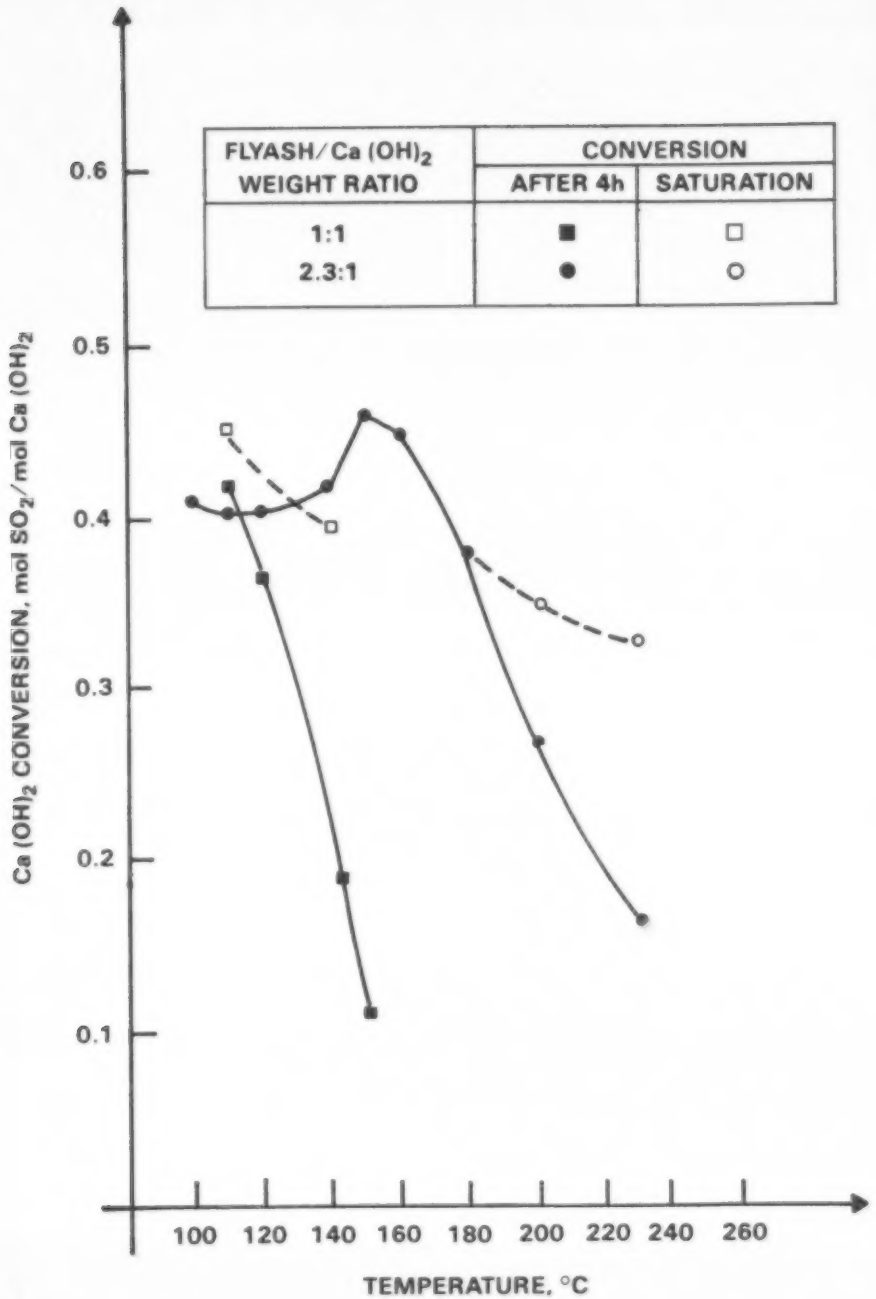


Figure 7-4. The effect of the temperature of pressure hydration on the reactivity of flyash/$Ca(OH)_2$ sorbents (sand-bed reactor conditions the same as in Figure 7-1).

temperature of pressure hydration of flyash and $Ca(OH)_2$ at the weight ratio of 2.3:1 seems to be 150 °C (302 °F), with conversion decreasing for hydrations in the range from 150 to 230 °C (302 to 446 °F).

7.2 PRESSURE HYDRATION OF DIATOMACEOUS EARTH/HYDRATED LIME MIXTURES

The previous screening of diatomaceous earth indicated that it was a more reactive source of silica than flyash and that lower siliceous-material-to-lime weight ratios were needed to activate lime for the removal of SO_2 (Section 5). Pressure hydration of diatomaceous-earth/CaO mixtures was examined at 150 and 230 °C (476 and 2,793 kPa) [302 and 446 °F (969 and 405 psi)] for moderate time periods of 1 and 1.25 h, respectively. The diatomaceous earth used was Filter Cel from Johns-Manville Products Corporation, which is about 87 percent SiO_2. The results for these mixtures are presented in Figure 7-5 for both pressure and atmospheric hydration. For the majority of conditions tested, no significant increase in conversion of $Ca(OH)_2$ was achieved by pressure hydration. Only at a weight ratio of Filter Cel to CaO of 1:1 did the conversion of $Ca(OH)_2$ increase from about 0.6 mol SO_2/mol $Ca(OH)_2$, for a sorbent atmospherically hydrated at 90 °C (194 °F) for 4 h, to 0.76 mol SO_2/mol $Ca(OH)_2$ for a sorbent pressure hydrated at 150 °C (320 °F) for 1 h. However, the rate of enhancement of $Ca(OH)_2$ conversion was much faster when pressure hydration was used. It took about 1 and 4 h, respectively, to produce a sorbent of comparable reactivity when pressure and atmospheric hydration were used. The insignificant difference between conversions for sorbents prepared by atmospheric and pressure hydration may be because diatomaceous earth, being much more reactive than flyash, reacts more quickly with lime than does flyash. If this is the case, most of the silica would react with lime under atmospheric hydration conditions, which are achieved prior to pressure hydration under constant volume heating. Some enhancement may be possible if diatomaceous earth and lime are pressure hydrated with additives, as described by Leineweber (1964).

7.3 DISCUSSION

Data presented above indicate that enhanced conversion of $Ca(OH)_2$ is possible within a feasible time period when pressure hydration is used instead of atmospheric hydration for preparing siliceous-material/lime sorbents. Contrary to what was observed during experimental work with atmospheric hydration of flyash with $Ca(OH)_2$, conversion of $Ca(OH)_2$ in the packed bed reactor did not

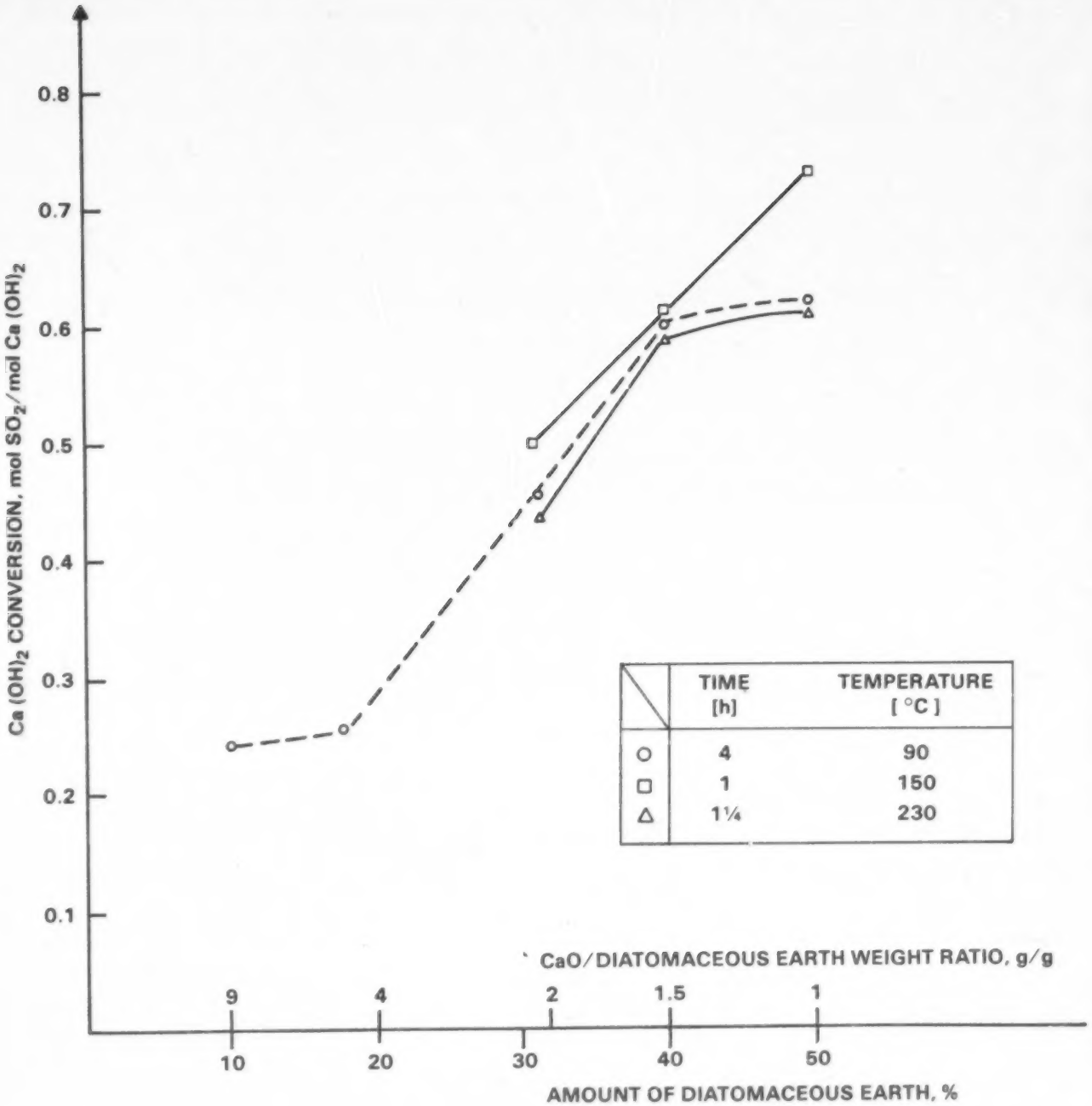


Figure 7-5. Combined effects of the temperature of pressure hydration and weight ratio of diatomaceous earth to CaO on the reactivity of the sorbent [sand-bed reactor conditions: relative humidity 60 percent, temperature 64 °C (147 °F), SO_2 concentration 1,000 ppm].

always increase with the time used for pressure hydration for a given temperature. Probably, because reaction silica was used rapidly as the result of high temperature/pressure conditions, the formation of calcium silicate hydrate which is reactive with SO_2 was stopped. It may be that this hydrate later crystallized into a less reactive one with a smaller surface area and less molecular water.

Figure 7-6 represents the correlation of the conversion of $Ca(OH)_2$ in the packed bed reactor and B.E.T. surface area of the flyash/$Ca(OH)_2$ samples pressure hydrated at different conditions of weight ratios, time, and temperature. This figure shows that the conversion of $Ca(OH)_2$ in the packed bed reactor correlated quite well with the measured B.E.T. surface area and that conversion increased with the increasing surface area of the sorbent. However, considerable data scatter in the conversion of $Ca(OH)_2$ in the packed bed reactor occurred for samples with B.E.T. surface areas in the range from 5 to 10 m^2/g. A more reactive phase of calcium silicate hydrate was probably formed at the weight ratio of flyash-to-$Ca(OH)_2$ of 2.3:1 rather than at 1:1. This was manifested by the fact that, for the same surface area, more $Ca(OH)_2$ was converted in the packed bed reactor for the sorbent produced by the pressure hydration of flyash and $Ca(OH)_2$ at a weight ratio of 2:3:1 rather than at 1:1. For example, the expected conversion of $Ca(OH)_2$ in the packed bed reactor would be about 0.35 and about 0.15 mol SO_2/mol $Ca(OH)_2$ for sorbents with a surface area of 5 m^2/g which were produced by pressure hydration of substrates at weight ratios of 2.3:1 and 1:1, respectively. Higher surface area sorbents were generally produced when a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1 was used rather than 1:1. The highest B.E.T. surface areas measured for sorbents prepared by pressure hydration at weight ratios of 2.3:1 and 1:1 were 29 and 14 m^2/g, respectively.

Three results for the sorbents prepared at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 by pressure hydration at 230 °C (2,793 kPa) [446 °F (405 psi)] do not correlate well with the other results using the same ratio. This seems to confirm Taylor's report (1964) claiming that, at such high temperature, anhydrous compounds (i.e., with small amounts of molecular water) are formed.

The development of sorbent surface area when pressure hydrating flyash with $Ca(OH)_2$ is provided in Figures 7-7 and 7-8. Figure 7-7 shows a sample of flyash and $Ca(OH)_2$ pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)] for 15 min. This sorbent had a B.E.T. surface area of 4 m^2/g, and in

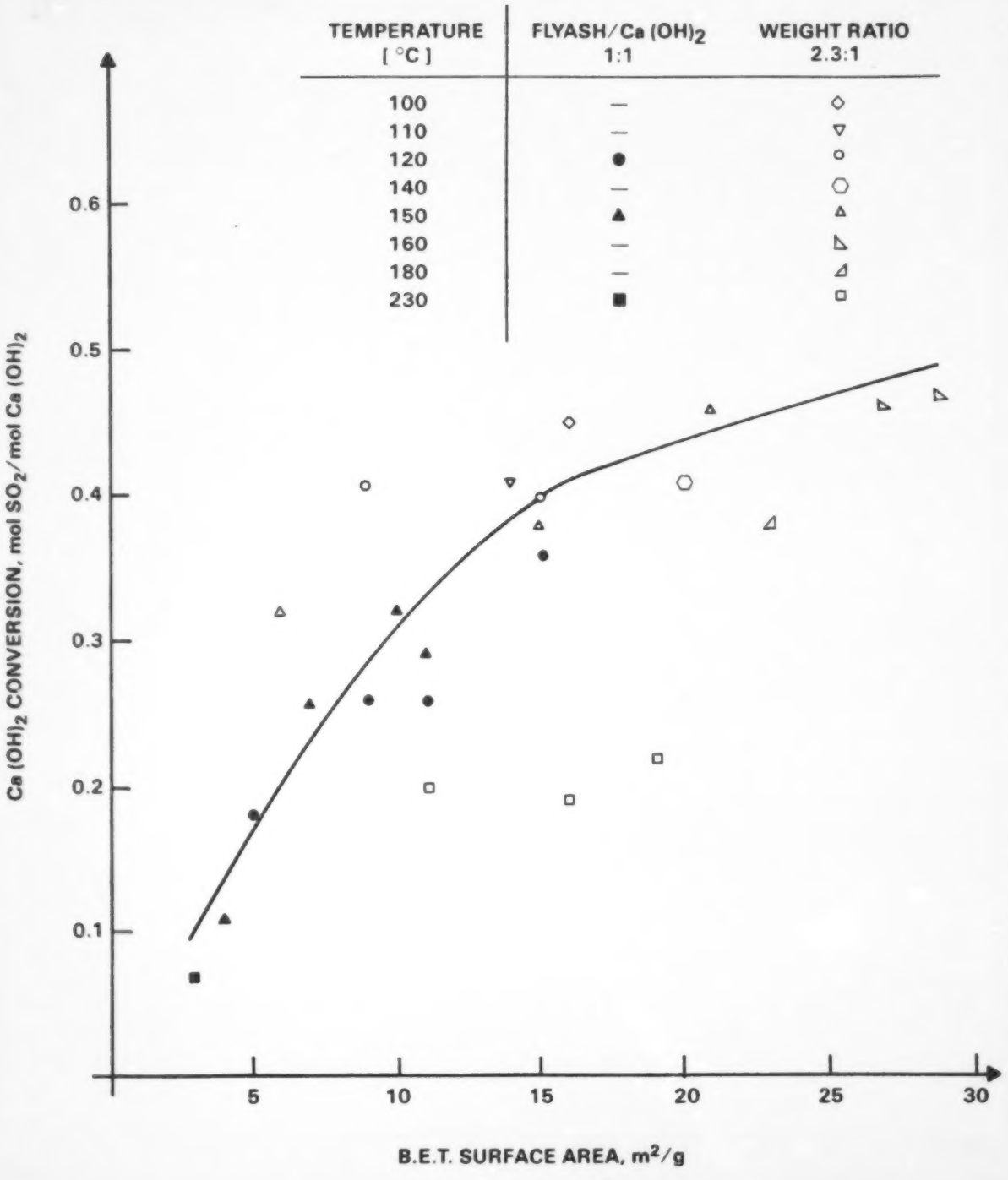


Figure 7-6. Correlation between measured B.E.T. surface area and the reactivity of flyash/$Ca(OH)_2$ samples (sand-bed reactor conditions the same as in Figure 7-1).

Figure 7-7. SEM photograph of sorbent at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 150 °C (302 °F) for 15 min (2,000x).

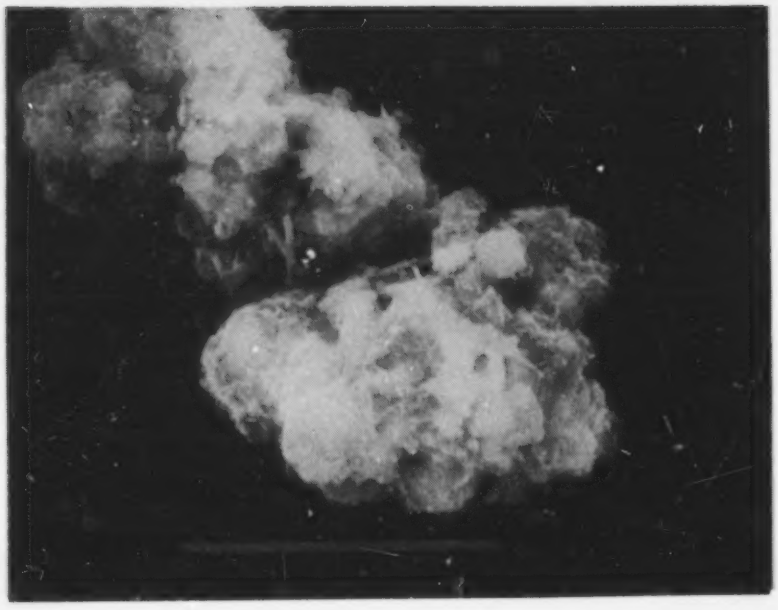


Figure 7-8. SEM photograph of sorbent at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 150 °C (302 °F) for 4 h (5,000x).

the packed bed reactor had a conversion of 0.17 mol SO_2/mol $Ca(OH)_2$. Flyash particles with quite smooth surfaces can be seen in Figure 7-7, as well as big chunks of $Ca(OH)_2$, indicating that the reaction of flyash with $Ca(OH)_2$ has hardly started. Figure 7-8 is quite different, showing a sorbent with the same weight ratio and pressure hydrated at the same temperature but for a longer period, 4 h. In this case, the measured B.E.T. surface area was 21 m^2/g, and the conversion of $Ca(OH)_2$ in the packed bed was 0.46 mol $SO_2/Ca(OH)_2$. No separate particles of $Ca(OH)_2$ and flyash can be seen in this sorbent; instead, a very well developed gel-like amorphous surface is evident in Figure 7-8, probably as a very thin layer since flyash particles can be seen underneath.

Figure 7-9 depicts the sorbent pressure hydrated at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1 at 230 °C (2,793 kPa) [446 °F (9,405 psi)] for 4 h. Even though the measured surface area was 17 m^2/g, the conversion of $Ca(OH)_2$ in the sand bed reactor was only 0.16 mol SO_2/mol $Ca(OH)_2$. When comparing Figures 7-8 and 7-9, different morphologies of the products are evident. Contrary to the gel-like amorphous material shown in Figure 7-8, a framework of distinct needle-shaped crystals is seen in Figure 7-9. The product in Figure 7-9 probably contains much less (or no) water of hydration that is needed for the sorbent to be reactive with SO_2, possibly explaining why this sorbent demonstrated poor reactivity in the packed bed reactor. This finding seems to be consistent with a report (Kalousek et al, 1954) which indicated that needle-like crystals of β-type calcium silicate were conversion products of ∝-type hydrates.

Still another morphology is evident in Figure 7-10, which shows the sample of flyash and $Ca(OH)_2$ pressure hydrated at a weight ratio of 1:1 at 150 °C (302 °F) for 4 h. This sorbent had a B.E.T. surface area of only 4 m^2/g, and the conversion of $Ca(OH)_2$ in the packed bed reactor was only 0.11 mol SO_2/mol $Ca(OH)_2$. Big platelet crystals, measuring several μm, can be seen in Figure 7-10, and the flyash spherules in Figure 7-11 indicate a poorly developed surface which is probably responsible for the low reactivity of this sorbent.

The results of the morphology study presented in Figures 7-7 through 7-11 suggest that two factors are necessary for a sorbent to readily react with SO_2 under the conditions encountered in a dry injection FGD process: large sorbent surface area and amorphous surface structure. Both factors can be

Figure 7-9. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1, pressure-hydrated at 230 °C (446 °F) for 4 h (2,000x).

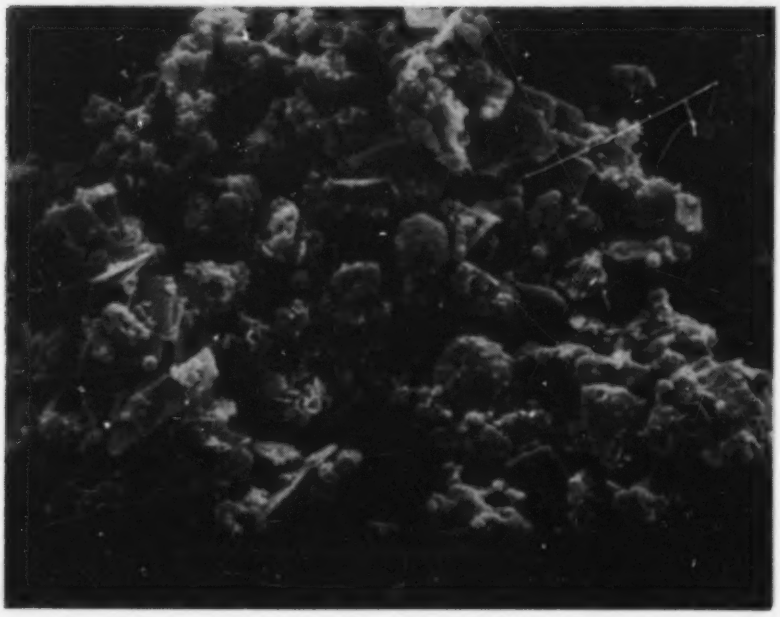


Figure 7-10. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 1:1, pressure-hydrated at 150 °C (302 °F) for 4 h (5,000x).

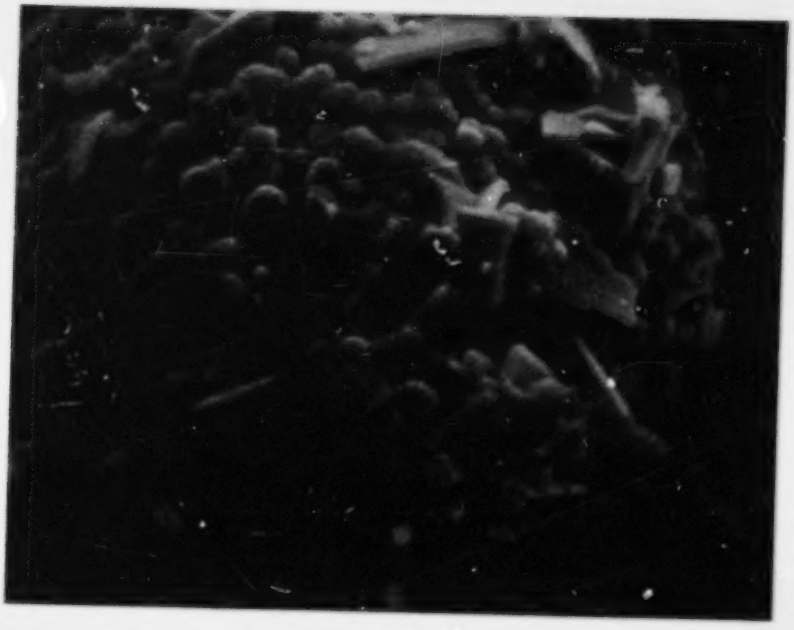


Figure 7-11. SEM photograph of sorbent prepared at a weight ratio of flyash to $Ca(OH)_2$ of 1:1, pressure-hydrated at 150 °C (302 °F) for 4 h (10,000x).

optimized by careful selection of the time/temperature conditions of pressure hydration for a selected flyash-to-$Ca(OH)_2$ weight ratio.

The results of a morphology study seem to be in good agreement with the x-ray diffraction measurements presented in Figure 7-12. Vertical lines in Figure 7-12 denote two-theta angles where $Ca(OH)_2$ peaks would appear. Section A of Figure 7-12 is a diffraction pattern of flyash and $Ca(OH)_2$ dry mixed at a weight ratio of flyash to $Ca(OH)_2$ of 2.3:1. Only peaks of $Ca(OH)_2$ and SiO_2 can be seen in this section (two major peaks of $Ca(OH)_2$ at 18 and 34° have intensities of about 250 and 350 counts/s, respectively). Section B of Figures 7-12 is a diffraction pattern for a sorbent with a flyash to $Ca(OH)_2$ ratio of 2.3:1, pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)] for 0.5 h. The intensity of $Ca(OH)_2$ peaks are significantly diminished compared with Section A (peaks at 18 and 34° were measured at 150 and 160 counts/s, respectively). This sorbent had a $Ca(OH)_2$ conversion of 0.32 mol SO_2/mol $Ca(OH)_2$ when exposed to SO_2 in the packed bed reactor operated at the normal experimental conditions. Section C of Figure 7-12 is a diffraction pattern of a sorbent with a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)] for 4 h. No peaks of $Ca(OH)_2$ can be seen in Section C and, when placed in the packed bed reactor under normal operating conditions, this sorbent had a $Ca(OH)_2$ conversion of 0.46 mol SO_2/mol $Ca(OH)_2$. Comparison of Sections A, B, and C of Figure 7-12 indicates that the conversion of $Ca(OH)_2$ increases proportionally to the disappearance of $Ca(OH)_2$, probably because of its use in forming a new phase of silica-enhanced sorbent. Section D of Figure 7-12 is a diffraction pattern of a sorbent pressure hydrated at 230 °C (2,793 kPa) [446 °F (405 °F)] for 4 h. This sorbent had a flyash-to-$Ca(OH)_2$ weight ratio of 2.3:1, and its packed bed reactor conversion of $Ca(OH)_2$ was 0.16 mol SO_2/mol $Ca(OH)_2$. A comparison of Sections C and D reveals that the hump at a two-theta angle of about 26° has an intensity of 40 and 20 counts/s, respectively. This hump is indicative of the amorphism of the sorbent and therefore suggests that the sorbent pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)] had a higher $Ca(OH)_2$ conversion in the packed bed reactor than the one hydrated at 230 °C (2,793 kPa) [446 °F (405 psi)], because its surface was significantly more amorphous.

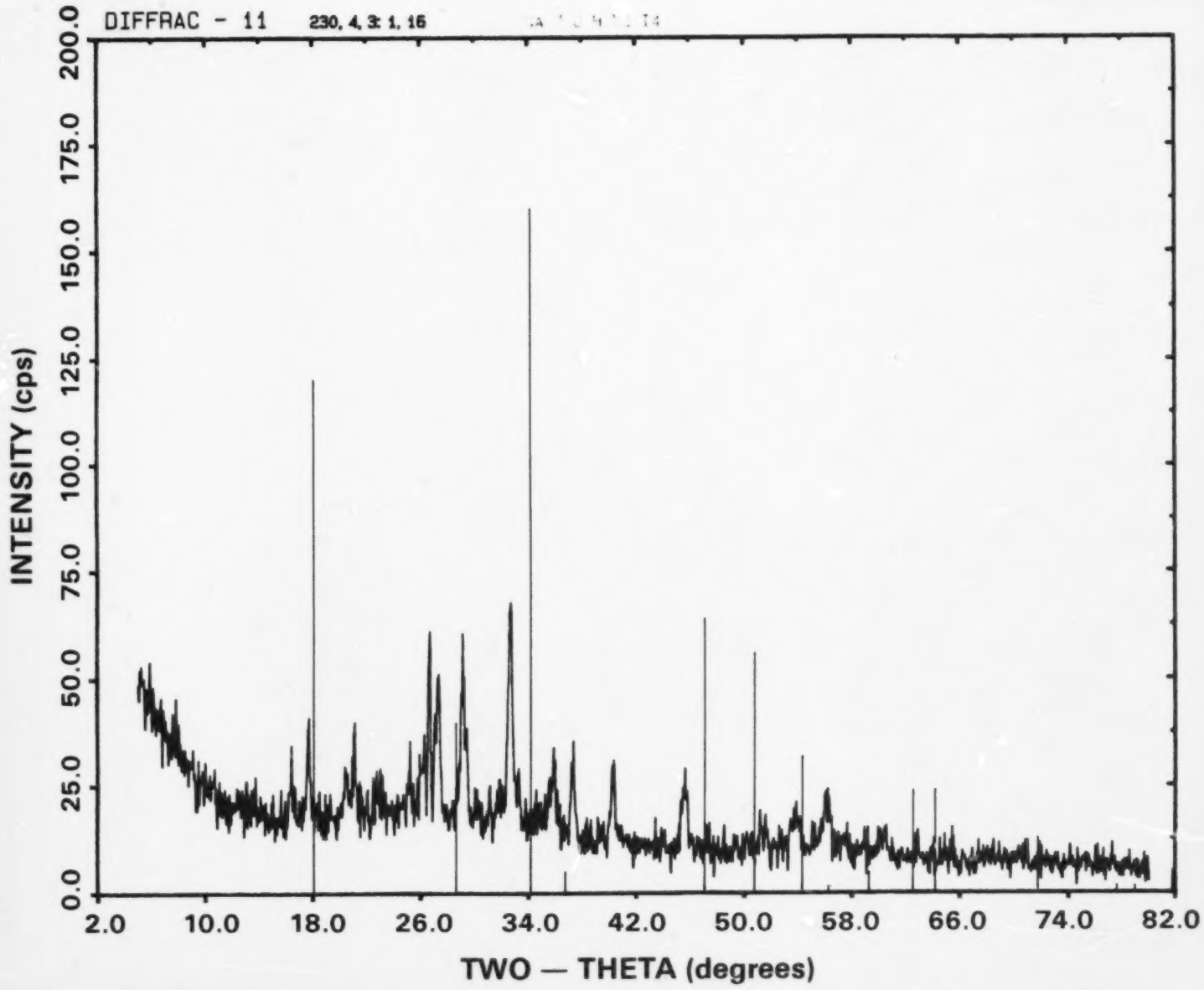


Figure 7-12a. X-ray diffraction patterns of sorbents at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1; reagents dry mixed.

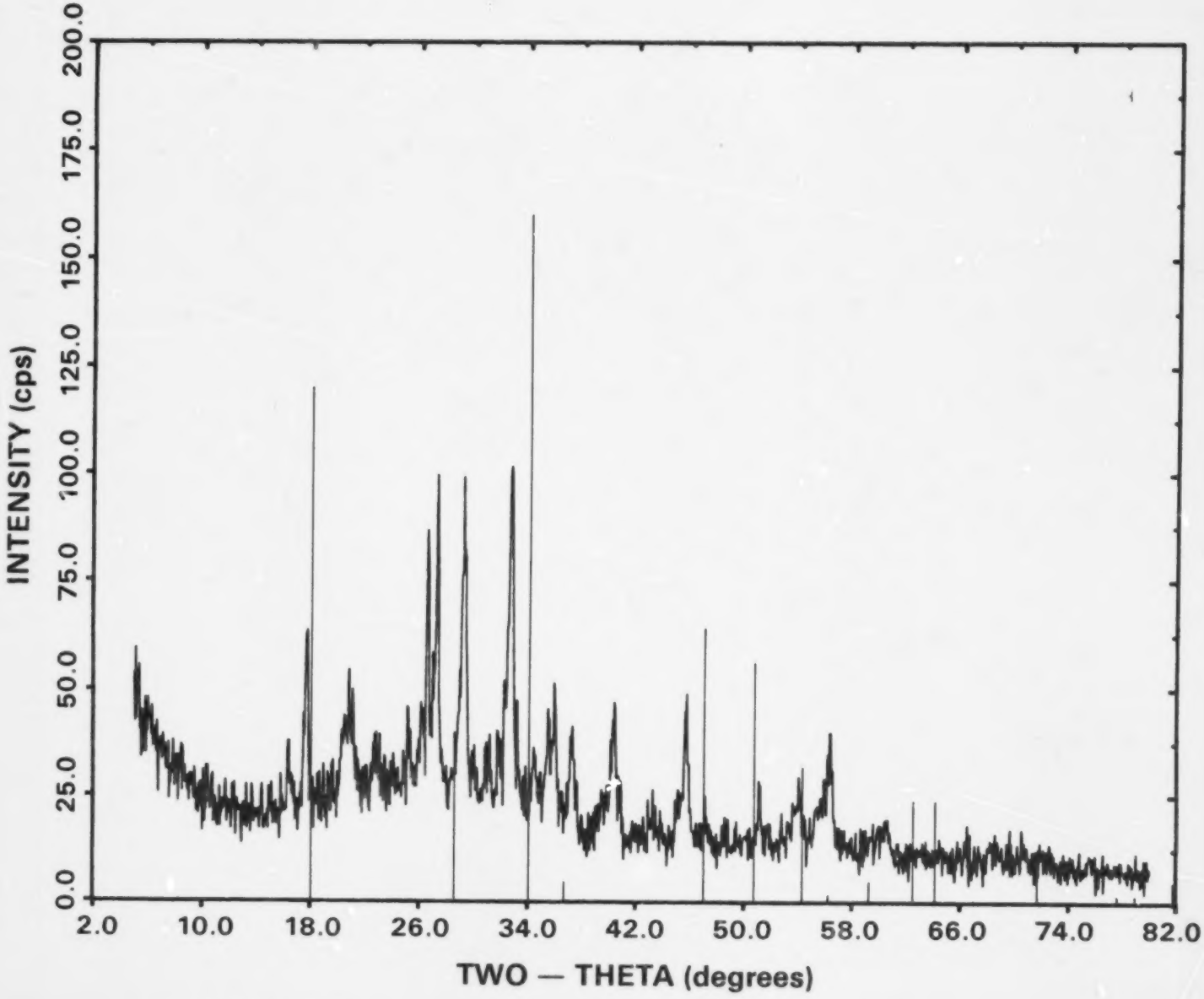


Figure 7-12b. X-ray diffraction patterns of sorbents at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1; reagents pressure hydrated at 150 °C (476 kPa) [302 °F (69 psi)] for 0.5 h.

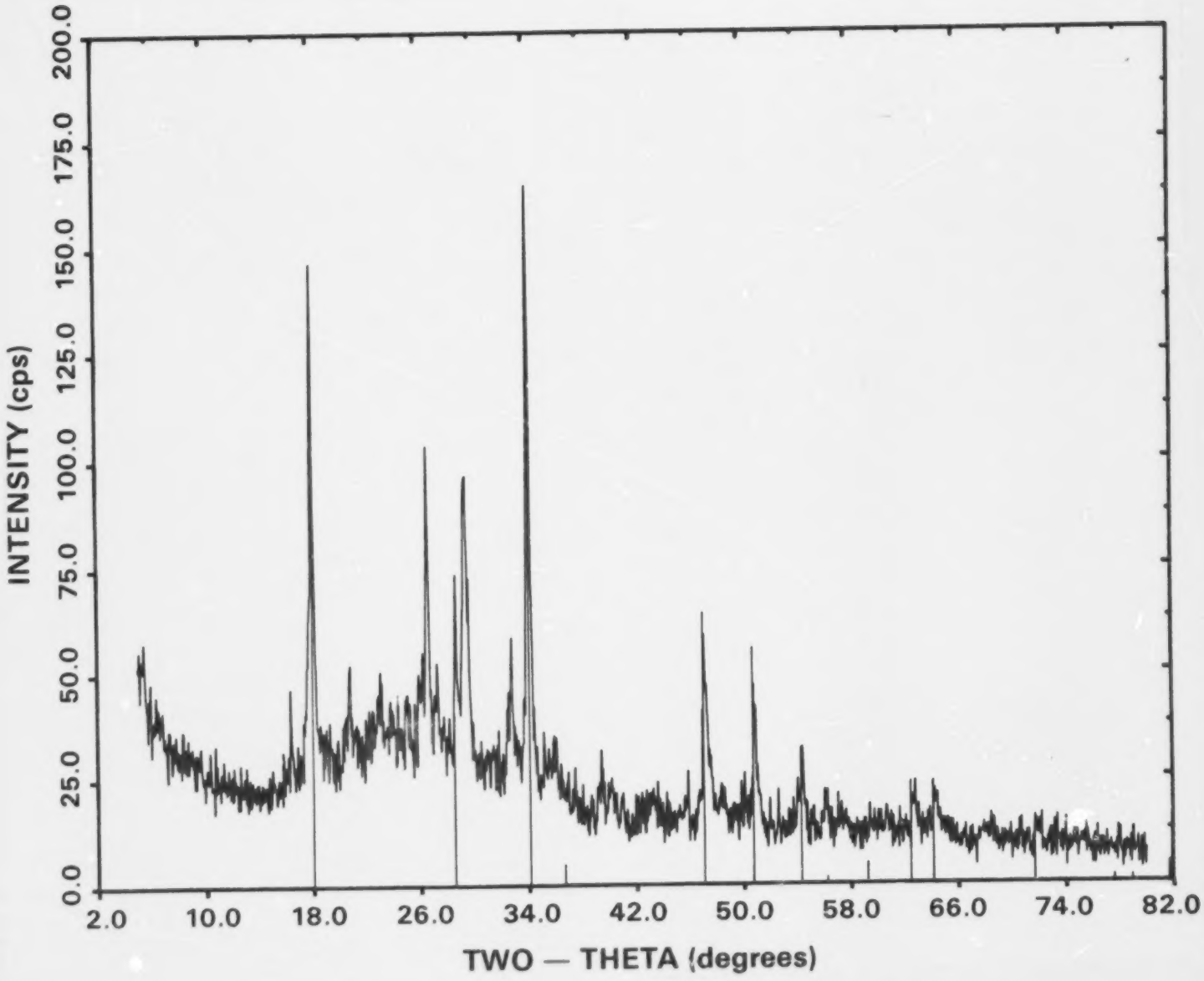


Figure 7-12c. X-ray diffraction patterns of sorbents at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1; reagents pressure hydrated at 150 °C for 4 h.

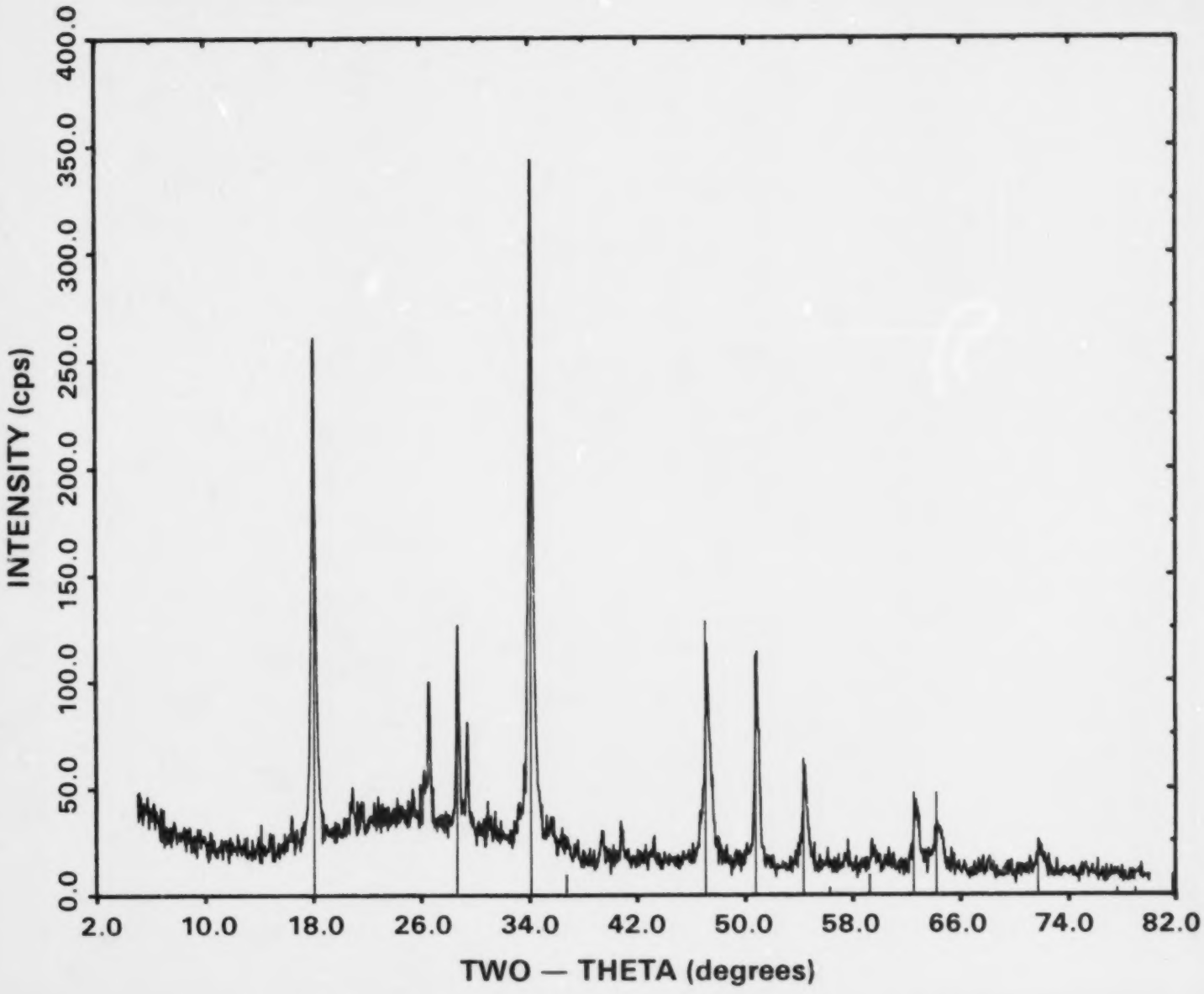


Figure 7-12d. X-ray diffraction patterns of sorbents at the weight ratio of flyash to $Ca(OH)_2$ of 2.3:1; reagents pressure hydrated at 230 °C (2793 kPa) [446 °F (405 psi)] for 4 h.

7.4 CONCLUSIONS

From this study, the following conclusions may be drawn:

1. Very reactive sorbents for the dry removal of SO_2 from flue gases can be produced by pressure hydration of mixtures of flyash or diatomaceous earth with lime.
2. Pressure hydration using flyash with lime fosters the formation of a sorbent which reacts with SO_2 in a much shorter time than does a similar sorbent prepared by atmospheric hydration.
3. Pressure hydration of diatomaceous earth with CaO does not offer any significant advantages over atmospheric hydration with respect to producing a reactive dry sorbent, which probably can be explained by the already quite high reactivity of the sorbent produced from diatomaceous earth with lime when atmospherically hydrated.
4. The conversion of $Ca(OH)_2$ in the packed bed reactor generally did not monotonically increase with the time of hydration for a given temperature of pressure hydration. After all the reactive silica was used, recrystallization probably took place and resulted in solids of lower reactivity with SO_2.
5. The conversion of $Ca(OH)_2$ in the packed bed reactor increased with the increasing weight ratio of flyash to lime. The conversion of $Ca(OH)_2$ was significantly enhanced by pressure hydration at the low weight ratios of flyash to $Ca(OH)_2$, which were ineffective in promoting conversion of $Ca(OH)_2$ in sorbents prepared by atmospheric hydration.
6. An optimum temperature range for the pressure hydration of flyash with $Ca(OH)_2$ was found to be between 110 and 160 °C (230 and 320 °F). The reactivity of the sorbent gradually decreased when pressure hydration was in the range 180 to 230 °C (356 to 446 °F).
7. The conversion of $Ca(OH)_2$ in the flyash-$Ca(OH)_2$ derived sorbent correlation well with B.E.T. surface area, increasing with increasing surface area.
8. SEM and x-ray diffraction studies demonstrated the formation of solids of different morphologies with different flyash/lime ratios and changing conditions of pressure hydration.

9. Comparison of packed bed reactor data and SEM morphology studies indicates that both high surface area, as well as amorphous surface structure, are necessary characteristics for the sorbent to be reactive with SO_2 at the flue gas conditions appropriate for the in-duct dry injection of sorbents.

SECTION 8

RECOMMENDATIONS

The following recommendations can be offered based on the results of this study:

A. Spent sorbent from furnace limestone injection shows low potential for downstream SO_2 capture unless reactivated by off-line slurrying at elevated temperatures. Significant improvement of SO_2 capture in the duct should be possible by dry injection of reactivated solids into pre-humidified duct. This could be achieved by the recycle/reactivation of the ESP particulate catch. Further work is needed to evaluate the technical and economic feasibilities of reactivated BLIS at the pilot and demonstration scales.

B. Calcium silicate hydrates were formed during the slurrying process of siliceous materials with hydrated lime. High reactivity of sorbents produced when using diatomaceous earth or bentomitic clay could partially be attributed to the large surface area of sorbent as well as its great water retaining capacity. Siliceous materials evaluated were mostly from the western U.S. which could add transportation costs if the east coast was the location of commercial application. Further work is needed to evaluate materials from known deposits in the eastern U.S. Additional work is also needed to optimize the preparation costs of the sorbent. Since a significant amount of energy would be required to dry the sorbent after it was hydrated, either blending of prepared slurry with dry recycled solids or pressure hydration could be used to produce solids feasible for duct injection. Pressure hydration of diatomaceous earth or bentomitic clay with hydrated lime was evaluated and did not offer significant reactivity or reaction time improvements over atmospheric hydration. Pressure hydrator would therefore be used here mosily as a means of producing dry solids for dry injection.

C. The enhancement of lime reactivity in flyash/hydrated lime and flyash/quicklime sorbents was possible by adding sodium hydroxide or phosphates during the atmospheric hydration. Further work is needed to evaluate the effect of additives during the pressure hydration.

D. The bench-scale data presented in this report revealed the potential of pressure hydration to lower the flyash/hydrated lime weight ratio and shorten the reaction time compared to atmospheric hydration reported before. The conversion of $Ca(OH)_2$ in the sand bed reactor generally did not monotomically increase with the time of hydration for a given temperature of pressure hydration. An optimum temperature range for the pressure hydration of the specific flyash with $Ca(OH)_2$ was found. At the same time SEM and x-ray diffraction studies demonstrated the formation of solids of different morphologies with different flyash/$Ca(OH)_2$ weight ratios and changing conditions of pressure hydration. The comparison of reactivity and morphology data revealed that both high surface area and amorphous surface structure are necessary for the sorbent to be reactive with SO_2 at the conditions tested. Significant amounts of further work is needed to fully optimize pressure, hydration time, temperature, flyash/$Ca(OH)_2$ weight ratio, and flyash type for dry injection SO_2 removal. Results available so far have demonstrated that pressure hydration can reduce sorbent preparation time from over 10 h to 1 to 2 h. The flyash/$Ca(OH)_2$ weight ratio could also be substantially reduced. possible further improvements could be found by using additives accelerating the reaction between flyash and $Ca(OH)_2$.

E. Only dry hydrated lime (reagent grade $Ca(OH)_2$) has been evaluated so far from the pressure hydration. Future work should include the use of quicklime. By using the heat of hydration of CaO, possible improvements of economics could be achieved. The effect of having CaO present initially rather than $Ca(OH)_2$ on the reactivity with SO_2 should also be investigated.

F. During the work reported in this report, the pressure hydrator was operated in the wet mode in which the final product was a thick paste, which needed to be dried before actual reactivity testing. Another mode of pressure hydrator operation should be tested, preferably on the

pilot scale. The desired mode of operation of the pressure hydrator would depend on the envisioned process layout. For example, for once through operation the dry mode of operation would be derived in which dry sorbent powder would be injected directly into the duct. With recycle, a wet mode could be used in which wet sorbent probe would be mixed with dry recycle solids, to produce solids feasible for the dry duct injection.

SECTION 9

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APPENDIX

QUALITY ASSURANCE DATA

QUALITY ASSURANCE DATA

A Quality Assurance Project Plan was issued for the reported Alkali Reactivity Bench Studies under EPA Contract No. 68-02-3988 in June 1985. The quality assurance objectives of this project were to assure that data collected during the bench-scale testing of sorbents for the dry injection FGD process were accurate and useful. Data obtained from this Level IV project are intended for use as guidelines for the selection of sorbents to be tested in the 50 and/or 2,000 acfm pilot plants.

The QA plan required that all measurement instruments be carefully calibrated. Where possible, accuracy was checked against calibration standards. Measured experimental data were entered on the data sheet shown in Figure A-1. The front page of the data sheet contained the information about the sample of sorbent tested, as well as parameters needed for the calculation of the sample's reactivity. The back page of the data sheet contained temperature parameters, recorded at 5 min intervals throughout the entire experiment (usually 60 min). The data recorded on the data sheet back page assured that the conditions in the reactor were representative of the intended experimental design.

DISCUSSION OF DATA QUALITY

The major measurements made in the Alkali Reactivity Bench Studies were SO_2 concentration in the simulated flue gas, water flow from the tank to the evaporation chamber (enforced by the syringe pump), process gas volumetric flowrate, process temperatures, and process pressures. The summary of measured parameters, their calibration methods and accuracy, is presented in Table A-1 along with the original goal for each type of measurement. In all cases, the accuracy of measurements made in the sand bed reactor's experimental set-up met or exceeded the quality assurance objectives listed in the Quality Assurance Project Plan (QAPP) developed for the project.

The accuracy of process temperatures and pressures, gas flow and water flow, and gravimetric measurements was determined from the calibration data. The high accuracy of the water flow (enforced by the syringe injection pump) should be pointed out. This parameter governed the relative humidity of the process gas. Experience has shown that the relative humidity of the gas is the process parameter of paramount importance. The accuracy of the SO_2 concentration, measured by an UV Spectrophotometric Analyzer, was also determined from the calibration data against the SO_2 span gas using a concentration

Test No.: Date
Absorbent Type
Additive
Sand Type
Syringe Type
Syringe pump gear type

Pressures: (mmHg)	Barometric	P_B	=
	Flowmeter	P_{FM}	=
	Reactor	P_R	=
	H_2O Vapor at Dry Bulb	P_{sat}	=
Temperatures: (°F)	Ambient	T_A	=
	Dry bulb	T_R	=
	Wet bulb	T_{wet}	=
Nitrogen:	Volumetric flow rate (as read)	F	=
	Standard volumetric flow rate (scfh)	F_o	=
	Molar flow rate (mol/h)	N	=
	Mass flow rate (g/h)	M	=
Pump setting		1/2	=
	nominal H_2O injection rate (g/h)	W_1	=
	H_2O collected (g/h)	W_2	=
Relative humidity:	nominal H_2O injection rate calc.	RH_1	=
	collected H_2O rate calc.	RH_2	=
	wet bulb measurement calc.	RH	
SO_2 inlet concentration (ppm)		CSO_2	=
fraction removed (1h)		R	=
SO_2 removed (1h) (mmol)		nSO_2	=
Amount of absorbent (g)		A	=
availability (fraction)		Y	=
molecular weight (g/mol)		MW_a	=
amount available (mmol)		N_a	=
Amount of Additive (g)		B	=
molecular weight (g/mol)		MW_b	=
Amount of Sand (g)		wt	=
SO_2 absorbed/mass unit absorbent (1h) (mol/g)			=
SO_2 absorbed/mol unit available absorbent (1h) (mol/mol)			=

FRONT FACE

Sand Bed Reactor Data Sheet

Time run: cylinder #:
H_2O collected: Pressure:
Bath Temp. :

Temp °F / Time min.	Dry Bulb	Inlet Gas	Wet Bulb	Evaporation Chamber
5				
10				
15				
20				
25				
30				
35				
40				
45				
50				
55				
60				

Comments:

BACK FACE

Figure A-1. Experimental data sheet.

Table A-1. Data Quality Summary

Measured Parameter (Method)	Calibration Method	Calibration Accuracy (%) Planned	Actual
SO_2 Concentration (UV Spectrophotometric)	SO_2 Span Gas	10	8
Process Pressures (U-Tube)	Hg U-Tube Manometer	2	—
Gas Flow (Rotameter)	Dry Gas Meter/ Stopwatch	5	—
Process Temperatures (K-Type Thermocouples or Hg-Thermocouples)	H_2O Phase Change	2	0.9
Water Flow (Syringe Injection Pump)	Graduated Cylinder/ Stopwatch	5	—
Weight (Analytical Balance)	Class S Weights	5	—

higher than that during the experiment. Typical recording of the calibration procedure for the SO_2 monitor is shown in Figure A-2. First, the adjustment of "zero" with nitrogen can be seen, followed by the monitor calibration with the SO_2 span gas. The "zero" measurement followed, and finally the actual concentration of SO_2 in the experimental simulated flue gas was measured.

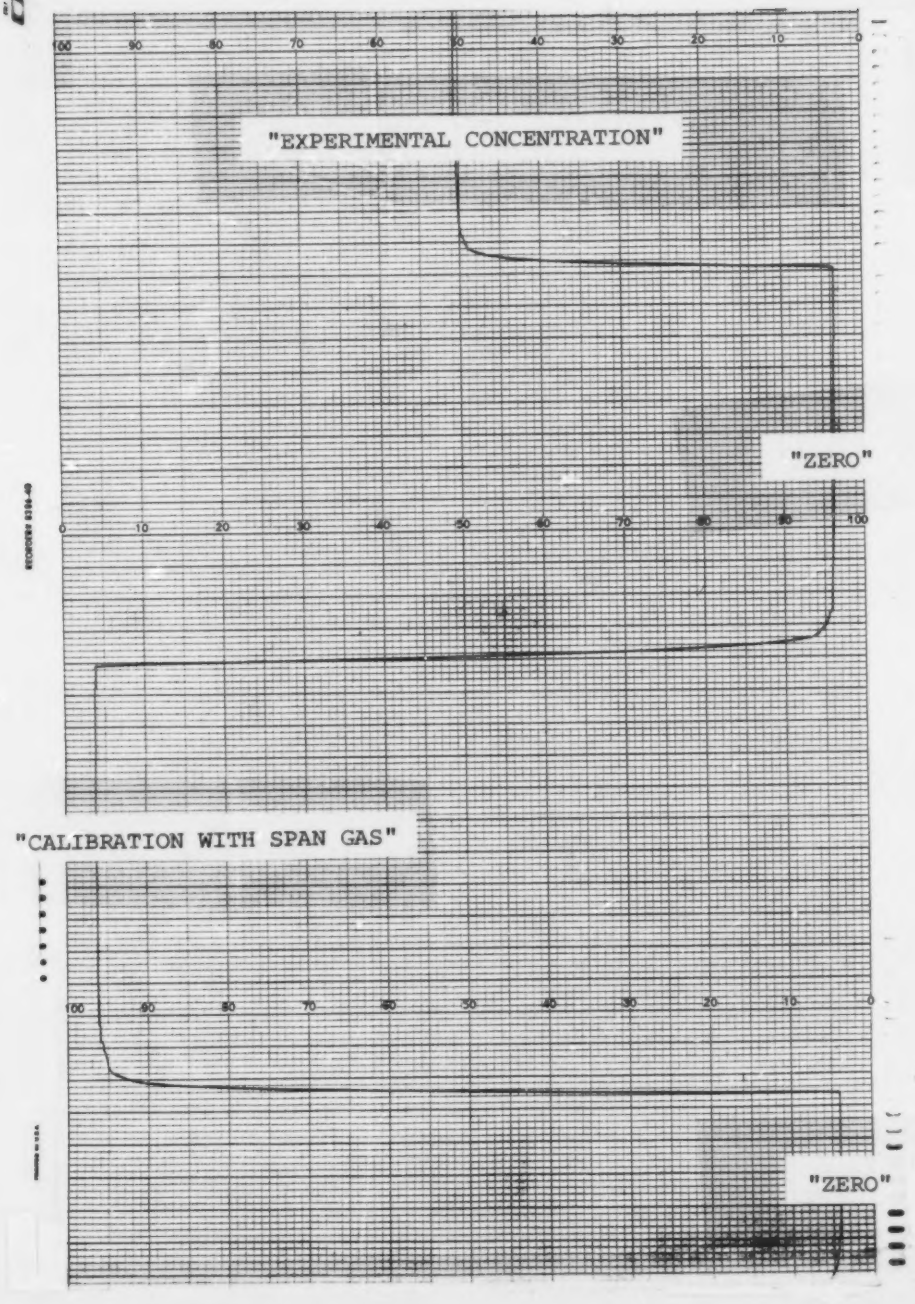

Figure A-2. Recording of the calibration procedure for the SO_2 monitor.